

CALCULATION OF ELECTRON BINDING ENERGIES

By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1977

ACKNOWLEDGEMENTS

The support and encouragment of my chairman, Prof. Yngve Öhrn, is gratefully acknowledged. During my stay at the Quantum Theory Project, he was of unfaltering assistance.

I would also like to thank all memebers of the Quantum Theory Project for providing a very stimulating atmosphere in which to work. Many valuable discussions were held with the faculty, post-docs and, in particular, other students.

I would also like to express my great appreciation for the constant support of my wife Bette Ackerman.

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Abstract of Dissertation Presented to the
Graduate Council of the University of Florida
in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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December 1977

Chairman: N. Y. Öhrn
Major Department: Chemistry

Contributions from relaxation and correlation effects are examined for ionization energies and electron affinities. A comparison is made of the Δ SCF and TOM methods showing that they are not the same through third order in Rayleigh-Schrödinger perturbation theory as had previously been thought. A direct method of obtaining values for ionization energies and electron affinities is proposed which includes the complete relaxation correction and an approximate correlation correction. This method is used to evaluate ionization energies for water and neon and to evaluate the electron affinity of lithium hydride. The results compare very favorably with both the experimental and other theoretical calculations.

Negative electron affinities are also studied. These quantities are given by electron scattering resonance energies. A method is derived to compute Harris phase shifts from which the resonance parameters can be obtained. The potentials used are static-exchange

potentials with and without the inclusion of an approximate polarization potential. Polarization effects are shown to be very important in applications to some representative Group IIA atoms.



Chairman

INTRODUCTION

The strength with which an electron is bound in a system, referred to as the binding energy, is a quantity which has received a great deal of interest in recent years, both from a theoretical and experimental viewpoint. Knowledge of such a quantity can be very useful in the study of chemical analysis and bonding. This fact has been demonstrated e.g. by K. Siegbahn in the development of ESCA (Electron Spectroscopy for Chemical Analysis). The study of electron binding energies can be broken down into the study of two main processes, electron detachment and electron attachment. The quantities measured in these processes are called the ionization energies and electron affinities respectively.

The ionization energy is the amount of energy required to completely remove an electron from a system. This can be obtained theoretically from the total energy differences between the N electron (usually neutral) initial state and the appropriate $N-1$ electron state. For atomic systems, this definition is unambiguous, but for molecular systems the ionization energies will depend on the inter-nuclear arrangements. When such a condition exists, there are two main types of ionization energies of interest experimentally and theoretically. These are known as the adiabatic and vertical ionization energies. The adiabatic ionization energy is given by the energy difference between states with each in its own equilibrium

geometry and the vertical ionization energy is obtained for a fixed nuclear arrangement, usually the equilibrium geometry of the initial N electron state. In Chapter 1 of this work, several methods of use today for calculating vertical ionization energies are explored. An attempt is made to analyze the various improvements and effects presently considered and to propose an alternative method which provides an accurate and efficient procedure by which ionization energies can be calculated. Applications of this method are given for both atomic and molecular systems.

The concept of electron affinity, or electron attachment, is very closely related to that of the ionization energy, or electron detachment, in that each can be thought of in terms of total energy differences. Electron affinities are usually defined as the total energy difference between the N electron parent system and the $N+1$ electron final system. This sign convention for electron affinities is such that if a positive result is obtained then the $N+1$ electron system is of lower energy and, hence, stable with respect to the initial system. As was the case for molecular ionization energies, there is the same distinction between adiabatic and vertical processes when referring to molecular electron affinities, with the vertical process still usually obtained at the geometry of the N electron parent. It is of interest to note that for atomic systems, the electron affinity of a given N electron state must be the same as an ionization energy of the resulting $N+1$ electron state. Chapter 2 is devoted to the analysis of methods used for obtaining positive electron affinities. It is shown that the same method that was developed for ionization

energies is also applicable to electron affinities and an example is given of such a calculation.

As of yet the possibility that the total energy of the $N+1$ electron final system will lie above that of the N electron parent, thus yielding a negative electron affinity, has not been mentioned. This possibility usually lies well outside the range of methods discussed so far and into the category of scattering processes. For most cases, the idea of a negative electron affinity is meaningless because the $N+1$ electron state is not stable and can, therefore, have any energy desired, depending only on the energy of the free electron. In some instances though, the concept of a negative electron affinity can have a meaning. Such a case is when, due to the shape of the potential which the "free" electron feels, the $N+1$ electron state has a non-negligible lifetime. The temporary negative ion state formed in this manner is known as a resonance and can be related to a specific energy value. The energy at which a resonance of this type occurs can then be used as the definition of the negative electron affinity. In Chapter 3 this type of binding is treated. A short review of the theory of electron-atom scattering resonances is given and a simple procedure is developed for the calculation of electron-atom scattering cross sections, from which such resonances can be obtained. This method is analyzed in terms of existing related methods and then applied to some representative Group IIA atoms to determine values of their negative electron affinities.

CHAPTER 1 IONIZATION ENERGIES

1.1 Discussion of Problem

As stated previously, the ionization energy of a system is the energy required to completely remove an electron. This can be given theoretically as the difference between the N electron and the N-1 electron system total energies. Experimentally, ionization energies can be determined via photoelectron spectroscopy. In such an experiment the system is bombarded by photons of a known energy, or equivalently frequency, and the kinetic energy distribution of the ejected electrons is measured. The electron binding energy I (ionization energy) can then be computed by Einstein's relation

$$I = h\omega - E_e,$$

where ω is the incident photon frequency and E_e is the ejected electron's kinetic energy. Both adiabatic and vertical energies can be detected by this technique. The adiabatic energy is measured from the band head in a spectrum and the vertical is measured relative to the band maximum. Several good reviews of photoelectron spectroscopy have been given by Siegbahn et al. (1967 and 1969), Turner et al. (1970), Eland (1974), and Price (1974).

One of the earliest and still most widely used methods for obtaining theoretical vertical ionization energies is known as Koopmans' theorem (Koopmans, 1933). The "Koopmans' theorem" states that the ionization energy is given by the negative of the Hartree-

Fock orbital energy, $-\epsilon$. It can be derived by first assuming a Hartree-Fock description of the N electron system and then allowing the same orbitals to approximate the $N-1$ electron state Hartree-Fock solutions. Discussions of the errors involved in the "frozen orbital" method have been given by Mulliken (1949) and Löwdin (1955a).

One seemingly obvious way of improving an ionization energy calculation is by improving the methods used to calculate total energies. Approaches of this type are called indirect methods since the quantity of interest (the ionization energy) is obtained from the results of two separate total energy calculations. Ab initio methods commonly used to calculate total energies for indirect methods include the Hartree-Fock method, Configuration Interaction, MC-SCF, or a variety of perturbation theory methods. All of these have the drawback that they require a high degree of accuracy since, in the last step, two very large numbers must be subtracted to obtain what is usually a quite small number. There also can be other even more serious problems with some indirect methods in ensuring that each state is calculated within the same level of approximation. This problem is addressed in greater detail in a later section.

A method capable of calculating the ionization energy directly via a single calculation would circumvent most of the problems mentioned for indirect calculations. Such methods are called direct methods. The two most common direct methods are the transition orbital method (Goscinski et al., 1973) and the electron propagator, or one-body Green's function (Linderberg and Öhrn, 1973). In following sections, the relationships between these methods and the more common indirect methods are discussed.

1.2 Relaxation Effects

In the Koopmans' ionization approximation, the orbitals obtained for the N electron state are assumed to remain unchanged by the ionization process. Clearly the potential felt by the remaining electrons is now different and the orbitals should be allowed to change (via reorganization or relaxation). One method of obtaining these reorganization effects is to perform an independent Hartree-Fock calculation for the $N-1$ electron state. The procedure by which the ionization energy is obtained from separate Hartree-Fock calculations is known as Δ SCF (Bagus, 1965). This technique can be used to define what is called the relaxation correction to Koopmans' theorem as the difference between the Δ SCF result and the Koopmans' result.

It should be mentioned at this point that the Hartree-Fock calculations referred to in this work are unrestricted Hartree-Fock calculations. Other types of Hartree-Fock methods, such as Roothaan's (Roothaan, 1960) or a projected Hartree-Fock (Löwdin, 1955b), may give different results and other interpretations from those discussed here.

Further non-relativistic corrections to the Koopmans' results not included in the relaxation correction are grouped together and called correlation corrections. These corrections can then be defined as the difference between the non-relativistic experimental result and the Δ SCF results. Figures 1 and 2, for water and furan respectively, show the relative importance of the relaxation and correlation corrections over an energy range from core ionization to outer valence ionization energies. It is evident from these figures that for core ionizations, the relaxation corrections can be quite large. In fact, they account for almost the entire difference between

Figure 1 Plot of relaxation and correlation corrections for water at each ionization energy. The corrections are shown near the respective energies with the correlation on the left and the relaxation on the right.

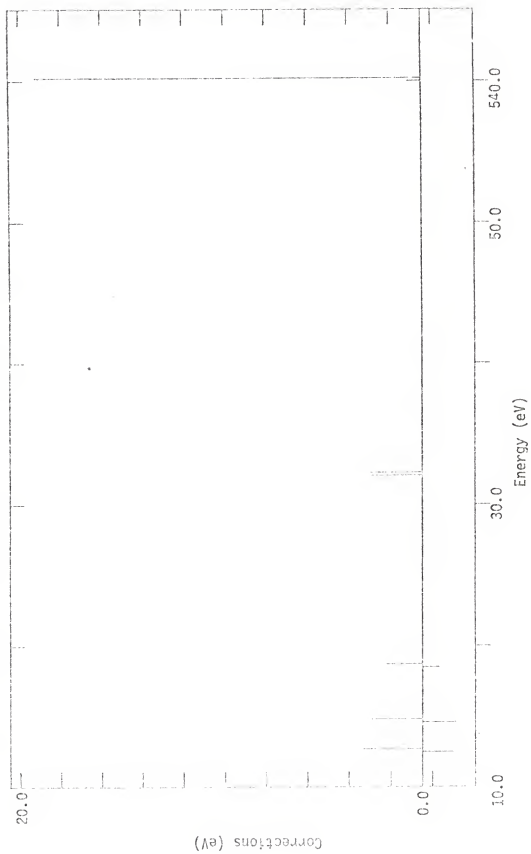
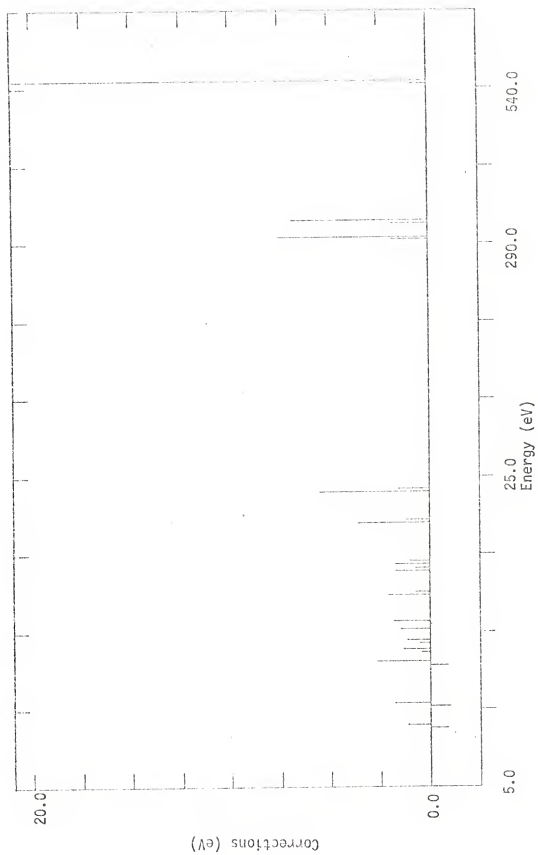


Figure 2 Plot of relaxation and correlation corrections for furan at each ionization energy. The corrections are shown near the respective energies with the correlation on the left and the relaxation on the right. The values were obtained from Hehenberger (1977).



the experimental and Koopmans' ionization energies and, therefore, the Δ SCF ionization energy will be very accurate. Although small the correlation contributions may be also important for the core in the calculation of chemical shifts. In the intermediate and valence regions, the correlation effects can be as important as the relaxation effects and possibly more important. Therefore, in these regions the Δ SCF ionization energy may not be very good. It is very interesting to note that for the systems examined here, the relaxation and correlation corrections for the outer valence level have almost equal magnitude but are opposite in sign. In cases such as this the original Koopmans' energy will be a better approximation than Δ SCF to the ionization energy.

To arrive at an explicit expression for the relaxation contribution, Rayleigh-Schrödinger perturbation theory can be used. The details of this procedure and its resulting expressions are given in Appendix A.

So far, only the indirect Δ SCF method has been discussed for calculation of ionization energies with the inclusion of relaxation effects. There is also a direct method designed to include the major relaxation contributions known as the transition operator method (TOM) (Goscinski et al., 1973). The ionization energy is given by this method as the eigenvalue, ϵ_X , of the "transition operator"

$$F_X^T = h + \sum_a \langle a | |a\rangle + \frac{1}{2} \langle X | |X\rangle .$$

To obtain an expression for the TOM correction to Koopmans' theorem which can be compared with the Δ SCF expression, Rayleigh-Schrödinger perturbation theory can again be used. Goscinski et al. (1975) pointed out that when perturbation theory is used to expand the transition

operator eigenvalue using the N electron ground state Hartree-Fock solutions as a reference, then the expressions obtained will differ from the Δ SCF expression in third order. But if the N and N-1 electron state total energy expressions are expanded with the TOM solutions as a reference, the Δ SCF expression will be equal to the TOM value through third order.

To demonstrate the techniques used and to check the results of Goscinski et al. (1975), both of these procedures were carried out. The first method, expanding the TOM eigenvalue, is demonstrated in Appendix B. By comparing the results obtained with the Δ SCF expression of Appendix A, the difference through third order is

$$\Delta\text{SCF} - \epsilon_X^T = \frac{1}{4} \sum_{l, k \neq a}^a \frac{\langle l|x|k\rangle\langle k|x|a\rangle\langle a|x|l\rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_a)} - \frac{1}{4} \sum_{l \neq a}^a \frac{\langle l|x|a\rangle\langle a|x|a\rangle\langle a|x|l\rangle}{(\epsilon_l - \epsilon_a)^2}.$$

This expression supports the statement by Goscinski that this procedure gives a non-zero difference in the third order expressions. The next procedure, where the total energies are expanded in TOM quantities and then subtracted, is demonstrated in Appendix C. The results found there can be stated as

$$(\Delta\text{SCF})^T - \epsilon_X^T = \frac{1}{4} \sum_{l, k \neq a}^a \frac{\langle T\tilde{x}|k\tilde{x}\rangle\langle k\tilde{x}|\tilde{a}\tilde{x}\rangle\langle \tilde{a}\tilde{x}|T\tilde{x}\rangle}{(\tilde{\epsilon}_l - \tilde{\epsilon}_a)(\tilde{\epsilon}_k - \tilde{\epsilon}_a)} - \frac{1}{4} \sum_{l \neq a}^a \frac{\langle T\tilde{x}|\tilde{a}\tilde{x}\rangle\langle \tilde{a}\tilde{x}|\tilde{a}\tilde{x}\rangle\langle \tilde{a}\tilde{x}|T\tilde{x}\rangle}{(\epsilon_l - \epsilon_a)^2},$$

where the tildes refer to TOM quantities. This result is clearly in contradiction with the result of Goscinski, who states that such a difference should be zero. It should be noted that if all the TOM orbitals and energies in the above expression are expanded in terms of the N electron state Hartree-Fock orbitals and energies, and then all terms of order higher than third are discarded, we arrive at the first expression obtained above.

Even though this work shows that the Δ SCF and TOM ionization energies are not identical, they have been found in the past to lie very close numerically. This should mean that the difference terms found here are fairly small. To demonstrate that this is true, in Table 1 the third order difference terms expressed in the Hartree-Fock orbitals are compared with the TOM and Δ SCF values obtained for the water molecule. For water, the difference terms are clearly small and will not cause a significant effect, with the possible exception of the $1a_1$ state.

1.3 Correlation Effects

Both of the previous methods discussed, TOM and Δ SCF, have included what was called relaxation effects but neither method was designed to take into account the remaining effects, called correlation effects. Correlation effects derive their name from the fact that in the Hartree-Fock approximation an electron sees the average, not the instantaneous, potential due to the other electrons. This means that there is no correlation between the motions of the electrons. As was shown in Figures 1 and 2, these neglected effects in theoretically determined ionization energies can be substantial, especially for the valence region.

Table 1
Comparison of Third Order Difference Terms
for Water (eV)

<u>Ionization</u>	<u>ΔSCF^a</u>	<u>TOM</u>	<u>3rd order diff.</u>
1a ₁	540.8	540.64	0.186
2a ₁	34.6	34.51	0.008
1b ₂	17.8	17.78	0.013
3a ₁	13.0	12.86	0.020
1b ₁	11.0	10.88	0.020

^a Δ SCF values from Goscinski et al. (1975)

There are several methods designed to include correlation effects in the calculation of total energies, thereby leading to indirect methods of calculating ionization energies. Perhaps the most widely used of those is the method of configuration interaction (CI). A very good review has recently been given on this subject by Shavitt (1977).

Calculating energy differences between states, particularly between states with different numbers of electrons, can be a very difficult matter using CI. In such cases, not only does one have to worry about choosing an orbital basis but a choice must also be made of many-electron functions (determinants or projected determinants) to be used. If possible, it would be preferable to use all the many-electron functions that could be generated from a chosen orbital basis. This would then guarantee that all possible correlation (obtainable with the orbital basis) had been included. Unfortunately, such CI's would be so large that they are impossible to perform in almost all cases of interest. Therefore, one must make selections of the many-electron basis resulting in approximations to the correlation energy. If extreme care is not taken in selecting the functions then the correlation effects may not be included for each state in a balanced manner.

In recent years, a direct method for calculation of ionization energies has emerged in quantum chemistry. This technique is known as the electron propagator (Linderberg and Öhrn, 1973). Reviews of this subject have been given by Hedin and Lundqvist (1969) in solid-state physics, Csanak et al. (1971) in atomic physics, Öhrn (1976) and Cederbaum and Domcke (1977) in molecular theory. To illustrate how

ionization energies are obtained, a short survey of some of the more important formulas and aspects of electron propagator theory will be given.

The electron propagator in spectral representation is given as

$$G_{pq}(E) = \lim_{\eta \rightarrow 0} \sum_s \left(\frac{f_s(p) f_s^*(q)}{E + E_O^N - E_S^{N+1} + i\eta} + \frac{g_s(p) g_s^*(q)}{E + E_S^N - E_O^N - i\eta} \right),$$

where g_s and f_s are the overlap amplitudes defined by

$$g_s(x) = \sum_i g_s(i) \cdot u(x) \quad \text{with} \quad g_s(i) = \langle N-1, s | a_i | N \rangle$$

$$\text{and} \quad f_s(x) = \sum_i f_s(i) \cdot u(x) \quad \text{with} \quad f_s(i) = \langle N | a_i | N+1, s \rangle.$$

These amplitudes can also be calculated via CI and could possibly give a mode of comparison between the two methods which is more sensitive than an energy criteria (Kurtz et al., 1976).

From the above expression for $\underline{G}(E)$, one can see immediately that the ionization energies are obtained as the poles of $\underline{G}(E)$ or the zeros of $\underline{G}^{-1}(E)$. One way of obtaining $\underline{G}$ is by solving the Dyson equation

$$\underline{G} = \underline{G}^0 + \underline{G}^0 \underline{\Sigma} \underline{G},$$

which can be rewritten

$$\underline{G}^{-1} = (\underline{G}^0)^{-1} - \underline{\Sigma}.$$

In these equations $\underline{G}^0$ is the propagator obtained for the unperturbed reference state. Usually this is the Hartree-Fock state and

$$(\underline{G}^{0-1})_{ij} = (E - \epsilon_i) \delta_{ij} ,$$

which leads to

$$(\underline{G}^{-1})_{ij} = (E - \epsilon_i) \delta_{ij} - \Sigma_{ij}(E) .$$

The terms $\Sigma_{ij}(E)$ are matrix elements of what is known as the self-energy.

If we assume we have an expression for $\Sigma_{ij}(E)$, then the problem is to solve for the zeros of the above energy dependent equation. One method of solving the equation is by a direct pole-residue search as described by Purvis and Öhrn (1974).

If only the diagonal element of $\underline{G}^{-1}$ is considered, it is evident that for E to be a solution it must obey the following relation:

$$E = \epsilon_i + \Sigma_{ii}(E) .$$

Solutions of this equation will also lead to improved values of ionization energies and this method has become known as the "quasi-particle" method.

1.4 Approximation of the self-energy

As was shown in the last section, to obtain improved ionization energies with respect to the Koopmans' value, an expression for $\Sigma_{ij}(E)$ is needed. A general expression for the self-energy has been given by Purvis and Öhrn (1974) in terms of a superoperator formalism (Goscinski and Lukman, 1970) as

$$\underline{\Sigma}(E) = (\underline{a}|\hat{H}f)(f|(E\hat{I} - \hat{H})|f)^{-1}(f|\hat{H}\underline{a})$$

The superoperators $\hat{I}$ and $\hat{H}$ are defined for any operator X by $\hat{I}X = X$ and $\hat{H}X = [X, H]_-$ (where H is the second quantized Hamiltonian)

and the binary product is defined as

$$(X_i | X_j) = \langle N | [X_i^\dagger, X_j]_+ | N \rangle ,$$

where $|N\rangle$ is a suitable reference state.

If the manifold $\underline{f}$ is chosen to be the set of fermion-like operators $\{a_p^\dagger a_b a_c, a_b^\dagger a_p a_q\}$, where the field operators are associated with the Hartree-Fock spin orbitals, this leads to

$$\begin{aligned} \Sigma_{ij}(E) = & \frac{1}{2} \sum_{apq} \sum_{a'p'q'} \langle pq || ia \rangle (\underline{M}^{-1})_{apq, a'p'q'} \langle ja' || p'q' \rangle \\ & + \frac{1}{2} \sum_{abp} \sum_{a'b'p'} \langle ab || ip \rangle (\underline{M}^{-1})_{abp, a'b'p'} \langle jp' || a'b' \rangle , \end{aligned}$$

where $\underline{M} = (f | (E\hat{I} - \hat{H}) | f)$. In the expression for $\underline{M}$, the Fock superoperator, $\hat{F}$, can be substituted for the Hamiltonian superoperator, $\hat{H}$. This is known as the Born collision approximation and causes $\underline{M}$ to be diagonal. The resulting self-energy is

$$\Sigma_{ij}(E) = \frac{1}{2} \sum_a \frac{\langle pq || ia \rangle \langle ja || pq \rangle}{E + \epsilon_a - \epsilon_p - \epsilon_q} + \frac{1}{2} \sum_{ab} \frac{\langle ab || ip \rangle \langle jp || ab \rangle}{E + \epsilon_p - \epsilon_a - \epsilon_b} .$$

Setting $E = \epsilon_i$ in the expression for $\Sigma_{ij}(E)$ gives

$$E = \epsilon_i + \Sigma_{ii}(\epsilon_i) ,$$

which is just the Rayleigh-Schrödinger perturbation theory expression for the correction to Koopmans' theorem. The alternative way of improving the Koopmans' value using the expression for $\Sigma_{ij}(E)$ was called the "quasi-particle" approximation and has been applied using

the second order expression given above (Hohlneicher et al., 1972). Both of these methods are well-known and give reasonable values for valence electrons..

Unfortunately, neither of the two previous methods are known to give accurate values for ionization energies of core electrons. The main reason for this is that the relaxation contributions are very large for core electrons and can not be adequately described by second, or even third, order perturbation theory of this type.

It was noted in second order (Pickup and Goscinski, 1973), and then extended to third order (Born et al., 1978), that $\Sigma_{ij}(\epsilon_i)$ can be conveniently separated into the Rayleigh-Schrödinger expressions for the relaxation and correlation corrections to Koopmans' theorem. This can be represented as

$$E = \epsilon_i + \Sigma_{ii}^R(\epsilon_i) + \Sigma_{ii}^C(\epsilon_i) .$$

The first two terms in the above equation can be identified as the Rayleigh-Schrödinger approximation to the Δ SCF ionization energy given in Appendix A. If instead of the approximate value, the exact value is used, the following equation is obtained

$$E = -I(\Delta\text{SCF}) + \Sigma_{ii}^C(\epsilon_i) .$$

This expression gives the correlation correction to the fully relaxed ionization energy and is the same in second order as the one given by Purvis and Öhrn (1976). This equation should now overcome the problem with the simple Rayleigh-Schrödinger expression and should provide excellent core ionizations. Since $-I(\Delta\text{SCF})$ is just a numerical value, it is possible to approximate it with the TOM

value. Even though the TOM ionization energy can be obtained from a single calculation, there is not any direct computational advantage in using it since a ground state calculation must always be done in order to obtain reference orbitals and energies.

An alternative approach to the one above is arrived at by making the relaxation-correlation separation in the original energy dependent expression for Σ ,

$$\Sigma_{ij}(E) = \Sigma_{ij}^R(E) + \Sigma_{ij}^C(E) .$$

If it is assumed that $\epsilon_i + \Sigma_{ii}^R(E)$ can still be approximated by the Δ SCF ionization energy, the following equation for E is obtained

$$E = -I(\Delta\text{SCF}) + \Sigma_{ii}^C(E) .$$

This approximation will be referred to as the "fully-relaxed quasi-particle" approximation by analogy to the previously mentioned "quasi-particle" approximation. The expression for the second order correlation correction is

$$\Sigma_{ii}^C(E) = \frac{1}{2} \sum_{\substack{a \neq i \\ p, q}} \frac{|\langle pq || ia \rangle|^2}{E + \epsilon_a - \epsilon_p - \epsilon_q} + \frac{1}{2} \sum_{\substack{a \neq i \\ b \neq i \\ p}} \frac{|\langle ab || ip \rangle|^2}{E + \epsilon_p - \epsilon_a - \epsilon_b}$$

1.5 Application to the Water Molecule

In order to make a comparison of the approximations to the ionization energy which have been discussed, they are applied to the water molecule. For this comparison two different basis sets were used to describe the molecule. The first, called basis I, is

a 14 CGTO combination of Dunning's oxygen basis (Dunning, 1970) and Huzinaga's hydrogen basis (Huzinaga, 1965). This basis is shown in Table 2. The other basis, basis II, is comprised of basis I plus a set of d-type GTO's on the oxygen with unit exponents and a set of p-type GTO's on each hydrogen, also with unit exponents. This augmented basis is used to give some check on the basis set effects of the approximations and to include functions which span all four irreducible symmetry representations of the C_{2v} molecule. The results obtained with each approximation are shown in Tables 3 and 4 for basis I and II respectively.

In the quasi-particle expression for the ionization energy,

$$E = \epsilon_i + \Sigma_{ij}(E) ,$$

if the "exact" self-energy expression is used, information about all ionizations can be obtained, not just the principle value related to the i^{th} Koopmans' energy. Even in the relaxed quasi-particle method with a second order approximate Σ^C , other ionization energies can be found with varying degrees of accuracy. These are approximate values for the "shake-up" processes which correspond to simultaneous ionization and excitation.

The method used to solve the relaxed quasi-particle equation for all the states listed in Tables 3 and 4, except the $2a_1$ states, is simple iteration with the Koopmans' value as a starting point. Convergence to 10^{-10} Hartrees was always very quick. For the $2a_1$ states, though, the iterative method converged to a value different than the one listed or it diverged. To explain this apparent anomaly it is helpful to look at a plot of E versus $-I(\Delta\text{SCF}) + \Sigma_{ij}^C(E)$ given

Table 2
14 CGTO Basis Used for Water

<u>orbital</u>	<u>exponent</u>	<u>coefficient</u>
sH	17.370	0.032828
	2.6273	0.23121
	0.58994	0.81724
s'H	0.16029	1.0
s0	7816.5	0.002031
	1175.8	0.015436
	273.19	0.073771
	81.17	0.2476
	27.184	0.61183
s''0	3.4136	0.2412
	9.5322	1.0
	0.9398	1.0
s'''0	0.2846	1.0
p0	35.183	0.01958
	7.904	0.12419
	2.3051	0.39473
	0.7171	0.6273
p'0	0.2137	1.0

Table 3
Water Basis I Results (eV)

state	KT	ΔSCF^a	TOM	2nd order RSPT	2nd corr ΔSCF	2nd corr TOM	ΔSCF q-part.	TOM q-part.	Exp ^b
1a1	559.44	540.8	540.64	529.77	541.0	540.81	541.0	540.85	540.2
2a1	37.04	34.6	34.51	33.12	34.4	34.26	32.8	32.73	32.2
1b2	19.52	17.8	17.78	18.01	18.7	18.66	18.7	18.67	18.6
3a1	15.43	13.0	12.86	12.64	13.8	13.61	13.8	13.63	14.7
1b1	13.78	11.0	10.88	10.52	11.8	11.65	11.8	11.68	12.6

^aGoscinski et al. (1975)

^bAlmlöf (1972)

Table 4
Water Basis II Results (eV)

state	<u>KT</u>	<u>ΔSCF</u>	<u>TOM</u>	2nd order RSPT	2nd corr ΔSCF	2nd corr TOM	ΔSCF q-part.	TOM q-part.	<u>Exp^a</u>
1a ₁	559.39	540.49	540.35	529.72	540.69	540.55	540.72	540.58	540.2
2a ₁	36.62	33.86	33.97	31.81	32.78	32.89	32.31	32.36	32.2
1b ₂	19.34	17.93	17.42	17.98	19.14	18.63	18.72	18.64	18.6
3a ₁	15.66	13.15	13.03	13.28	14.30	14.18	14.33	14.21	14.7
1b ₂	13.67	10.89	10.75	10.87	12.06	11.92	12.09	11.95	12.6

^aAlmlöf (1972)

if Figure 3 for basis I and Figure 4 for basis II. It can be seen that because of the poles of $\Sigma_{ij}^C(E)$ which exist in the region shown, there are actually three solutions. Two of the solutions are quite close (one of which is the primary solution) and this is the source of the problems in the iterative procedure. Table 5 shows the values obtained for the principle ionization and two shake-ups in the region.

Table 6 shows a comparison of the results of this work with those of Cederbaum et al. (1973) and Hubac and Urban (1977). The results of Cederbaum were obtained by solving the Dyson equation with second and third order self-energies. The basis used was the same as basis II except the hydrogen p-like GTO's had exponents of 0.75. The results of Hubac and Urban are Rayleigh-Schrödinger results for both second and third order using a basis similar to basis I. The results of the Δ SCF-relaxed quasi-particle method in second order are clearly better than the previous second order results and compare favorably with the third order results. It is worth noting that neither Cederbaum nor Hubac and Urban have reported any results for the $1a_1$ ionization where relaxation effects dominate.

1.6 Application to the Neon Atom

As a further test of the methods discussed for the calculation of ionization energies, the neon atom is chosen. Since it is an atom, it has the advantage when comparing with experiment of not having vibrational fine structure. There has also been a great deal of related work done on neon (Purvis and Öhrn, 1976) and, therefore, it provides a good check. The basis set used for the

Figure 3 Plot of $-I(\Delta\text{SCF}) + \Sigma_{ij}^{\text{SCF}}(E)$ versus energy for water obtained with basis I. A second order self-energy was used and the ΔSCF -relaxed quasi-particle solutions are the intersections with the 45° line.

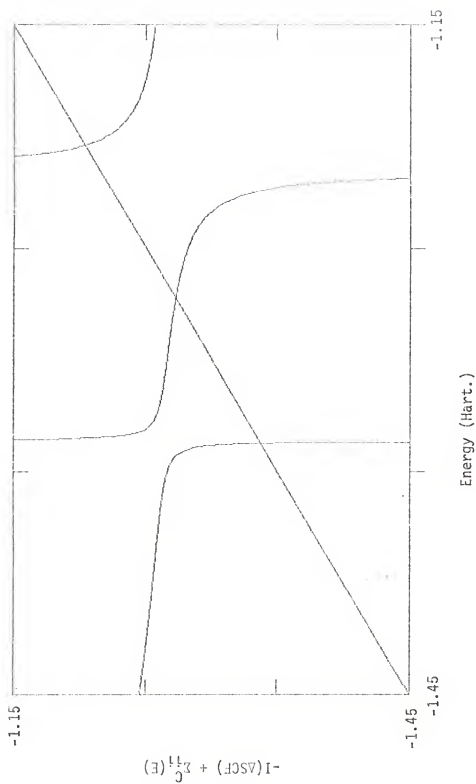


Figure 4 Plot of $-I(\Delta\text{SCF}) + \Sigma_{11}^C(E)$ versus energy for water obtained with basis II. A second order self-energy was used and the ΔSCF -relaxed quasi-particle solutions are the intersections with the 45° line.

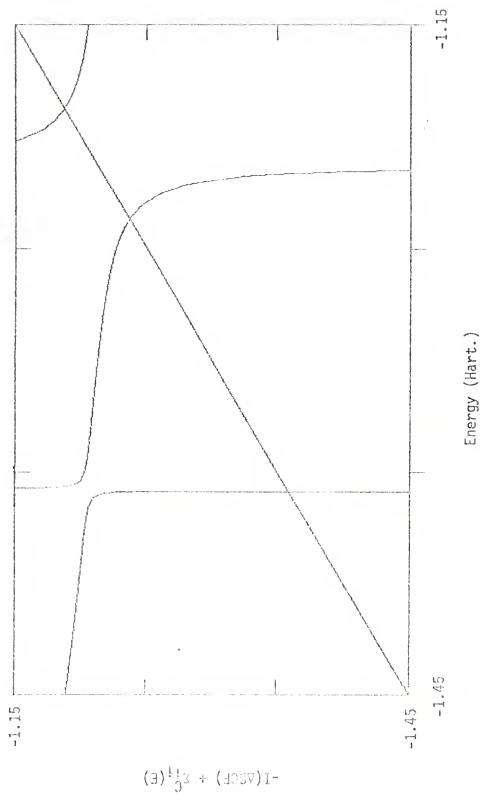


Table 5
Ionizations in 30-40 eV range

<u>designation</u>	<u>basis I</u>	<u>basis II</u>
principle $2a_1$	32.76	32.31
shake-up	34.62	33.66
shake-up	36.39	36.96

Table 6
Comparison of Results (eV)

<u>State</u>	<u>Ced2^a</u>	<u>Ced3^b</u>	<u>HU2^c</u>	<u>HU3^d</u>	<u>BI^e</u>	<u>BII^f</u>
2a ₁	32.93	35.10	33.38	35.22	32.8	32.31
1b ₂	17.70	19.22	17.93	19.42	18.7	18.72
3a ₁	13.18	15.18	12.62	14.74	13.8	14.33
1b ₁	10.92	13.03	10.48	12.75	11.8	12.09

^aSecond order results of Cederbaum (1973).

^bThird order results of Cederbaum (1973).

^cSecond order results of Hubac and Urban (1977).

^dThird order results of Hubac and Urban (1977).

^e Δ SCF-relaxed quasi-particle results with basis I.

^f Δ SCF-relaxed quasi-particle results with basis II.

neon calculations is shown in Table 7 and the results obtained are shown in Table 8.

As can be seen, excellent results were obtained for both the second order corrected TOM and the TOM-relaxed quasi-particle approximations. These results are also compared to the second order corrected TOM approximation of Purvis and Öhrn (1976) and they compare very well. The discrepancy in this work for the 2s level can be explained as a basis set effect. This discrepancy is removed in the work of Purvis and Öhrn (1976) where they used the same basis except that a 2s orbital replaced the 1s (8.91407) orbital.

Table 7
Neon STO Basis

<u>orbital</u>	<u>exponent</u>
1s	8.91407
1s	9.5735
1s	15.4496
2s	7.7131
2s	4.7746
2s	2.8462
2s	1.0000
2p	4.4545
2p	2.3717
2p	1.470
2p	0.750
3d	2.80

Table 8
Neon Results (eV)

<u>State</u>	<u>KT^a</u>	<u>10M</u>	<u>2nd order corr. 10M</u>	<u>10M-relax. q-part.</u>	<u>Exp.</u>	<u>p80^b</u>
1s	892.18	868.82	869.07	869.07	869.12	869.28
2s	52.64	49.17	47.64	47.76	48.21	48.19
2p	23.11	20.53	21.58	21.56	21.56	21.02

^aKoopmans' Theorem
^bPurvis and Öhrn (1976)

CHAPTER 2 POSITIVE ELECTRON AFFINITIES

2.1 Discussion of Problem

A positive electron affinity represents the decrease in total energy a system attains with the addition of an electron. Analogous to ionization energies, there are two different types of electron affinities, vertical and adiabatic. The adiabatic electron affinities are also known as the thermodynamic electron affinities. Methods of obtaining electron affinities can be broken down into three classes: experimental, theoretical, and empirical fitting. There are numerous methods which fall into the classes of experimental and empirical fitting and a discussion of these is outside the scope of this work. A very good discussion of many of these methods is given by Steiner (1972).

One problem common to almost all methods, theoretical and non-theoretical, is the very small size of electron affinities. The largest known electron affinity is 3.82 eV for CN (Berkowitz et al., 1969). This presents special problems for the indirect theoretical methods where the N and $N+1$ electron total energies are used.

In the next section, an analysis of the contributions to the electron affinity is made in a similar manner to that used for ionization energies. An attempt is made to obtain explicit expressions for these contributions as before.

2.2 Analysis of Effects

The simplest theoretical method for calculating electron affinities is Koopmans' theorem. The theorem is the same as it was for ionization energies, except now the negative of the first unoccupied orbital energy is used. Relaxation and correlation corrections can again be defined in terms of the Δ SCF electron affinity. The perturbation expressions derived in Chapter 1 for ionization energies can be applied to electron affinities if the $N+1$ electron state is used as the reference state. Clearly this is not what is desired. It would be most useful if expressions in terms of the N electron reference state were obtained so that the corrections to the Koopmans' electron affinity could be calculated with the same quantities as are used to calculate corrections to the Koopmans' ionization energy.

To find an expression for the relaxation correction to Koopmans' electron affinity, Rayleigh-Schrödinger perturbation theory is again used. The following treatment will parallel closely what is done in Appendix A.

The expression for the Δ SCF electron affinity is

$$\begin{aligned} -EA(\Delta\text{SCF}) &= E_{\text{HF},x}^{N+1} - E_{\text{HF}}^N \\ &= \tilde{\epsilon}_x + \sum_a \{ \tilde{\epsilon}_a - \epsilon_a \} - \sum_a \langle \tilde{a} \tilde{x} | | \tilde{a} \tilde{x} \rangle - \frac{1}{2} \sum_{a,b} \{ \langle \tilde{a} \tilde{b} | | \tilde{a} \tilde{b} \rangle - \langle \tilde{a} \tilde{b} | | \tilde{a} \tilde{b} \rangle \}. \end{aligned}$$

In the above expression and the following derivation, the "tilded" quantities will refer to the $N+1$ electron state. When these $N+1$ electron state quantities are expanded in terms of the N electron state quantities and only terms of third order or less are kept, the

following expression is obtained

$$\begin{aligned}
 -EA(\Delta SCF) = & \epsilon_x + \epsilon_x^{(1)} + \epsilon_x^{(2)} + \epsilon_x^{(3)} \\
 & + \sum_a \{ \epsilon_a^{(1)} + \epsilon_a^{(2)} + \epsilon_a^{(3)} \} \\
 & - \sum_a \{ \langle ax || ax \rangle + \langle a^{(1)}_x || ax \rangle + \langle ax || a^{(1)}_x \rangle \\
 & + \langle a^{(2)}_x || ax \rangle + \langle ax || a^{(2)}_x \rangle + \langle a^{(1)}_x || a^{(1)}_x \rangle \\
 & + \langle ax^{(1)} || ax \rangle + \langle ax || ax^{(1)} \rangle + \langle ax^{(2)} || ax \rangle \\
 & + \langle ax || ax^{(2)} \rangle + \langle ax^{(1)} || ax^{(1)} \rangle \} \\
 & - \sum_{a,b} \{ \langle a^{(1)}_b || ab \rangle + \langle ab || a^{(1)}_b \rangle + \langle a^{(2)}_b || ab \rangle \\
 & + \langle ab || a^{(2)}_b \rangle + \langle a^{(1)}_b || a^{(1)}_b \rangle \} \\
 & - \frac{1}{2} \sum_{a,b} \{ \langle a^{(1)}_b^{(1)} || ab \rangle + \langle ab || a^{(1)}_b^{(1)} \rangle \\
 & + \langle a^{(1)}_b || ab^{(1)} \rangle + \langle ab^{(1)} || a^{(1)}_b \rangle \} .
 \end{aligned}$$

In order to simplify this expression, the form of the perturbation must be known. This can be found by considering the relation between the Fock operators

$$F_x^{N+1} = F^N + \langle \tilde{x} || \tilde{x} \rangle + \sum_a \{ \langle \tilde{a} || \tilde{a} \rangle - \langle a || a \rangle \}$$

By using this perturbation to find expressions for $\epsilon_a^{(1)}$ and $\epsilon_x^{(1)}$, it can be shown that they will cancel many of the integral terms as they did in the ionization expression. It can also be easily shown that $\epsilon_x^{(2)}$ and $\epsilon_x^{(3)}$ vanish through third order. This leaves

$$\begin{aligned}
 -EA(\Delta SCF) = & \epsilon_x + \sum_a \{ \epsilon_a^{(2)} + \epsilon_a^{(3)} \} - \frac{1}{2} \sum_{a,b} \{ \langle a^{(1)} b^{(1)} | | ab \rangle \\
 & + \langle ab | | a^{(1)} b^{(1)} \rangle + \langle a^{(1)} b | | ab^{(1)} \rangle + \langle ab^{(1)} | | a^{(1)} b \rangle \}
 \end{aligned}$$

By inserting into this expression the RSPT equations for the orbital and orbital energy corrections and simplifying, the following result is obtained

$$\begin{aligned}
 -EA(\Delta SCF) = & \epsilon_x - \sum_{\substack{a \\ k \neq a}} \frac{|\langle ax | | kx \rangle|^2}{(\epsilon_k - \epsilon_a)} \\
 & + \frac{1}{2} \sum_{\substack{a,b \\ k \neq a \\ l \neq b}} \left\{ \frac{\langle ax | | kx \rangle \langle kl | | ab \rangle \langle bx | | lx \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} \right. \\
 & + \frac{\langle ax | | kx \rangle \langle kb | | al \rangle \langle lx | | bx \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} \\
 & + \frac{\langle al | | kb \rangle \langle bx | | lx \rangle \langle kx | | ax \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} \\
 & \left. + \frac{\langle ab | | kl \rangle \langle lx | | bx \rangle \langle kx | | ax \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} \right\} \\
 & + \sum_{\substack{a \\ k,l \neq a}} \frac{\langle lx | | kx \rangle \langle kx | | ax \rangle \langle ax | | lx \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_a)} \\
 & - \sum_{\substack{a \\ l \neq a}} \frac{\langle lx | | ax \rangle \langle ax | | ax \rangle \langle ax | | lx \rangle}{(\epsilon_l - \epsilon_a)^2}
 \end{aligned}$$

If this expression is now compared to the one obtained for $-I(\Delta SCF)$ in Appendix A, it is seen to be identical except for the signs on some of the terms. It is interesting to note that the number of times the perturbation $\langle x | | x \rangle$ appears in a term can be correlated with

the sign difference. If $\langle x | | x \rangle$ appears an even number of times, the signs are different, and if it appears an odd number of times, the signs are the same.

It is fortunate that this sign change occurs in the ΔSCF expression, at least in second order. By subtracting the second order relaxation expression from the full second order self-energy obtained previously, the correlation correction to the relaxed electron affinity is obtained. It is given by

$$\Sigma_{xx}^C = \frac{1}{2} \sum_{\substack{a \\ p,q \neq x}} \frac{|\langle pq | | xa \rangle|^2}{\epsilon_x + \epsilon_a - \epsilon_p - \epsilon_q} + \frac{1}{2} \sum_{\substack{a,b \\ p \neq x}} \frac{|\langle ab | | xp \rangle|^2}{\epsilon_x + \epsilon_p - \epsilon_a - \epsilon_b}.$$

It should be noted that this is the same correlation expression that was used to obtain ionization energies. The only difference is that now the virtual orbital sums are restricted instead of the occupied sums. This means that the program written to evaluate the RSPT correlation correction and the relaxed quasi-particle correction for ionization energies can also be used to obtain the similar quantities for electron affinities.

2.3 Application to LiH

The molecule LiH was chosen as a test case mainly because it is well characterized by previous work (Jordan et al., 1976). Two different basis sets were used to perform the calculations at an equilibrium distance of 3.015 a.u. One basis is a 19 STO basis, shown in Table 9, and the other is a 13 CGTO basis, shown in Table 10. The results of the calculations are shown in Table 11.

Table 9
LiH 19 STO Basis

<u>orbital</u>	<u>exponent</u>
1sLi	4.6990
1sLi	2.5212
2sLi	1.2000
2sLi	0.7972
2sLi	0.6000
2sLi	0.3000
2pσLi	2.7500
2pσLi	1.2000
2pσLi	0.7369
2pσLi	0.6000
2pσLi	0.3000
2pπLi	0.7369
2pπLi	0.3500
1sH	1.5657
1sH	0.8877
2sH	1.3765
2sH	0.4000

Table 10
LiH 13 CGTO Basis

<u>orbital</u>	<u>exponent</u>	<u>coefficient</u>
sLi	642.41895	0.09214
	96.79849	0.01621
	22.09109	0.07732
	6.20107	0.24579
	1.93512	0.47019
sLi	0.63674	0.34547
	2.19146	0.03509
	0.59613	0.19123
sLi	0.07455	1.00000
sLi	0.02079	0.39951
	0.00676	0.70012
	0.08948	1.00000
pLi	2.19146	0.00894
	0.59613	0.14101
	0.07455	0.94535
pLi	0.08948	0.15559
	0.02079	0.60768
	0.00676	0.39196
	0.00676	0.39196
sH	18.73110	0.03349
	2.82539	0.23473
	0.64012	0.81376
sH	0.16128	1.00000

Table 11
LiH Electron Affinity Results (eV)

<u>basis</u>	<u>KT^a</u>	<u>ΔSCF</u>	<u>TOM</u>	<u>2nd corr. ΔSCF</u>	<u>ΔSCF-relax. q-part.</u>
13CGTO	0.204	0.237	0.236	0.256	0.256
19ST0	0.198	0.238	-----	0.287	0.287

^aKoopmans' theorem value.

These results agree very well with the result of 0.2986 eV of Jordan et al. (1976) using Simon's EOM method (Simons and Smith, 1973). The fact that the STO result is better than the GTO result is evidence that the STO basis is a much more complete basis in the region of the maximum of the charge distribution of LiH^- . As another check on the quality of the basis sets, the dipole moment was calculated from the Hartree-Fock orbitals. A value of 6.11 D was obtained for the GTO basis and 6.02 D for the STO basis, compared to an experimental value of 5.88 D.

CHAPTER 3 NEGATIVE ELECTRON AFFINITY

3.1 Resonances

As was mentioned previously, the study of negative electron affinities is embodied in the study of electron scattering. In recent years, considerable amounts of work have been done on the calculation of resonances in electron scattering with both atomic and molecular targets and several excellent reviews have been given by Burke (1968), Taylor (1970), Schulz (1973), and Nesbet (1975). Following the definitions of Taylor (1970), resonances (also called "temporary negative ions" or "compound states") can be separated into three main classifications; core excited types I and II and single particle resonances.

Core excited type I (C.E. I) resonances are also called Feshbach or hole-particle resonances. Such resonances are formed when the incoming electron excites a target electron into an excited orbital, lessening the screening of the nuclear field. The electron then gets trapped in this potential and the resonance acts as a bound state relative to the excitation threshold. These resonances can be viewed as being caused by the excited state having a positive electron affinity. C.E. I resonances are usually the narrowest, thereby longest lived, of the three types.

Core excited type II (C.E.II) resonances are very similar to C.E. I resonances. The difference is that they lie above the

excitation threshold. The resonance is formed by trapping the incoming electron inside a centrifugal barrier set up by the combination of its angular momentum component and the potential well induced by the electron when it excites and polarizes the target. Since such a resonance is caused by the shape of the potential, it is given the classification of a shape resonance, and because it depends on the $l(l+1)/(2r^2)$ term in the potential, we expect to see resonances only for p and higher partial waves.

The final type of resonances are called single particle resonances. They, like C.E. II resonances, are shape resonances. The difference from C.E. II resonances lies in that there is no target excitation. Energetically, single particle resonances lie just above the ground state and well below excitation thresholds. It is these single particle resonances that can be identified as defining the negative electron affinity of a system. Until recently, this type of shape resonance has been very difficult to detect, both experimentally and theoretically. In the last year or so, Burrow et al. (1976) have performed low energy electron transmission experiments in which they have detected such resonances in the Group IIA elements Mg, Zn, Cd, and Hg.

3.2 Methods for Calculating Cross Sections

In order to detect broad single particle shape resonances theoretically, the electron scattering cross section must be calculated. Most methods of use in scattering calculations today can be divided into two main types, numerical integration methods and algebraic methods. The numerical integration methods are exemplified by the

close-coupling method (Burke, 1968). The subject of algebraic methods has been extensively reviewed by Truhlar et al. (1974) and Harris and Michels (1971). For bound state calculations an analogous classification of methods can be made. In this case, the numerical Hartree-Fock method (Froese, 1963) is the analogue of the close-coupling method and the matrix Hartree-Fock methods are the analogues of the algebraic methods. Experience from bound state problems has shown that as the complexity of the problem is increased in going from atomic to molecular systems, the algebraic methods are much more useful than the numerical integration methods. It is anticipated that a similar trend will exist in scattering problems as the complexity increases, for example by having many coupled equations to solve or by using non-spherical potentials.

The early algebraic methods were given by Hulthén (1944), Kohn (1948), and again Hulthén (1948) (also given by Rubinow (1955)). All three of these methods had the problem of giving spurious resonances, called pseudoresonances. In 1967, Harris caused renewed interest with the proposal of a method for single channel scattering (Harris, 1967). Nesbet (1968) was the first to analyze the source of the spurious results in the early methods and proposed the anomaly-free method for single channel scattering. The anomaly-free method was later extended to multichannel scattering (Nesbet, 1969) and also Harris and Michels generalized the Harris method and extended it to multichannel problems in the minimum-norm method (Harris and Michels, 1969). The method chosen in this work for the calculation of shape resonances is the simple Harris method. The reasons for this choice are brought out in the following brief derivation of the method.

As has been demonstrated (Hedin and Lundqvist, 1969) the wavefunction for the scattered electron is a solution of the formally exact equation

$$h(x)\Psi(x) + \int \Sigma(x, x'; E)\Psi(x')dx' = E\Psi(x) ,$$

where Σ is a complex nonlocal potential known as an "optical potential" and h is a single particle operator composed of the kinetic energy and nuclear attraction operators. Since only electron-atom scattering is to be considered, the central potential allows a separation of variables in spherical polar coordinates to be made. By also making a partial wave expansion of Ψ (Roman, 1965), the above equation reduces to the following radial equation

$$\left\{ \frac{d}{dr^2} + \frac{1(1+1)}{2r^2} + V(r) \right\} \phi_1(r) = E\phi_1(r) ,$$

where $E = \frac{1}{2}k^2$ with k being the momentum of the scattered electron. For convenience, the notation

$$L = \frac{d^2}{dr^2} + \frac{1(1+1)}{2r^2} + V(r)$$

is used. It should be kept in mind that L , through $V(r)$, is in general nonlocal, energy dependent, and complex.

The function ϕ_1 is assumed to be of the form $s_1 + tc_1 + \sum b_i u_i$, where s_1 and c_1 asymptotically are solutions to the radial equation with $V = 0$, namely the regular and irregular spherical Bessel functions $j_1(kr)$ and $n_1(kr)$. The explicit forms of s_1 and c_1 are discussed later. The set of functions $\{u_i\}$ is any suitable L^2 set of basis functions which go to zero both asymptotically and at the origin. By using

this form for ϕ_1 , t can be identified as $\tan\delta_1$, where δ_1 is the phase shift of the 1th partial wave.

In order to solve for δ_1 , the condition that the projection of $(L - E)\phi_1$ on the set of L^2 functions vanish,

$$(u_i | L - E | \phi_1) = 0 \text{ for all } u_i ,$$

is required to be satisfied. Upon substitution for ϕ_1 , this leads to

$$(u_i | L - E | s_1) + t(u_i | L - E | c_1) + \sum_j b_j (u_i | L - E | u_j) = 0 .$$

A vast simplification can be obtained by choosing the L^2 functions to be eigenfunctions of the operator L . This assumption then gives

$$(u_i | L - E | s_1) + t(u_i | L - E | c_1) + b_i(E_i - E) = 0 .$$

By fixing the value of E to be equal to the eigenvalue corresponding to u_i and rearranging, the sought after expression for δ_1 is obtained as

$$\tan\delta_1 = - \frac{(u_i | L - E_i | s_1)}{(u_i | L - E_i | c_1)} .$$

This is the expression given for the Harris phase shift (Harris, 1967).

One major advantage in calculating Harris phase shifts, over other algebraic methods, is that only integrals containing one continuum function need be calculated. A very obvious disadvantage to this method is that phase shifts can be determined only at energies corresponding to the positive eigenvalues of L . If the system being considered is small enough so that a large basis set can be used, the restriction to eigenvalues of L creates no problem.

The partial cross section can be calculated from the phase shift via the relation

$$\sigma_l = \frac{4\pi}{k^2} \sin^2 \delta_l (2l + 1) .$$

A total elastic cross section can then be obtained by summing the partial cross sections

$$\sigma = \sum_l \sigma_l .$$

Therefore, all that is now needed to calculate elastic cross sections is a form for the potential $V(r)$ in L .

3.3 Choice of Potential

One simple choice for a potential is the Hartree-Fock (or static-exchange) potential. This corresponds to letting the operator L be the Fock operator,

$$L = h + \sum_i \langle \phi_i | | \phi_i \rangle .$$

With this potential, the expansion functions u_i and scattering energies E_i are the virtual Hartree-Fock orbitals ϕ_i and orbital energies ϵ_i . Finding the phase shifts at the positive orbital energies now corresponds to the evaluation of the following integrals

$$(\phi_i | T_l - E_i | S) = (\phi_i | \frac{Z}{r} | S) + \sum_j^{\text{occ}} (\phi_j \phi_j | | \phi_i S) ,$$

where S is either s_l or c_l .

The functions s_l and c_l , as mentioned earlier, should go asymptotically as j_l and n_l respectively, but they should also go to zero at the origin. Therefore, the actual forms used for these

functions are

$$s_1 = j_1(kr)$$

$$c_1 = j_{1+1}(kr) + \left(\frac{1+1}{kr}\right)j_{1+2}(kr) .$$

This particular choice of c_1 is due to Armstead (1968) and it has the advantage that all the integrals needed will only involve regular spherical Bessel functions. A description of how to evaluate the necessary integrals is given by Harris and Michels (1971).

In the static-exchange method, the target potential is only weakly affected by the incoming electron through the exchange terms. In addition to exchange effects, polarization effects have been shown to be very important in electron scattering (Truhlar et al., 1971). For elastic scattering on atoms an important polarization effect is the charge induced-dipole polarization, which for large r behaves as

$$V_{pol}(r) \sim \frac{-\alpha}{2r^4} .$$

Such a form for the polarization potential can not be used because of the unphysical singularity at the origin and several alternate forms have been suggested. The one chosen for this work is

$$V_{pol}(r) = \frac{-\alpha}{2r^4} \quad r > r_0$$

$$\frac{-\alpha r}{2r_0^5} \quad r < r_0 ,$$

where α is the static polarizability and r_0 is a cutoff parameter. The role of r_0 is to cut off the attractive polarization potential before it penetrates the charge distribution of the atom. More is said later about how to pick the parameter r_0 .

Using the above potential, the operator L is now

$$L = F + V_{\text{pol}}.$$

With this choice of L , we can no longer use the Hartree-Fock orbitals and orbital energies as the expansion functions and scattering energies. To obtain new functions and energies, the eigenvalue problem $\underline{L}\underline{C} = E\underline{C}$ must be solved. Using the Hartree-Fock orbitals as a basis for solving this problem leads to the simplification of $\underline{L}$ such that $\underline{L} = \underline{\epsilon} + \underline{V}_p$, where $\underline{\epsilon}$ is a diagonal matrix of Hartree-Fock orbital energies and $(\underline{V}_p)_{ij} = (\phi_i | V_{\text{pol}} | \phi_j)$. Once the solutions have been found in terms of the Hartree-Fock orbitals, they can be back transformed to the primitive basis giving the desired orbitals and energies to proceed in finding the phase shifts.

3.4 Relation to Other Methods - Helium Test Case

In order to evaluate the results of the method developed, the relationships between it and two other methods, namely those of Harris and Michels (1971) and Yarlagadda et al. (1973), are explored. In the method of Harris and Michels, the target is described by the N electron determinantal (CI) solutions of the full N electron Hamiltonian,

$$\Gamma = \sum_{\mu} a_{\mu} \Gamma_{\mu} | D_{\mu}^N \rangle.$$

The scattering solution is then given by solutions to an $N+1$ electron Hamiltonian, H_{N+1} , written as

$$H_{N+1} - E = (H_N - E_{\Gamma}) + (T_1 - \frac{1}{2}k^2) + \sum_{j=2}^{N+1} \left(\frac{1}{r_{1j}} - \frac{1}{r_1} \right)$$

The solution is assumed to be of the form $\phi_S + t\phi_C + \sum_i b_i \eta_i$, where the functions ϕ_S , ϕ_C , and η_i are $N+1$ electron determinantal functions given by

$$\phi_S = \sum_{\mu} a_{\mu\Gamma} |SD_{\mu}^N\rangle ,$$

$$\phi_C = \sum_{\mu} a_{\mu\Gamma} |CD_{\mu}^N\rangle ,$$

$$\text{and } \eta_i = \sum_{\mu} b_{\mu i} |D_{\mu}^{N+1}\rangle ,$$

where $|CD_{\mu}^N\rangle$ and $|SD_{\mu}^N\rangle$ are $N+1$ electron determinants. The equation for the Harris phase shift is then

$$\tan\delta = \frac{-\langle \eta_i | H_{N+1} - E_i | \phi_S \rangle}{\langle \eta_i | H_{N+1} - E_i | \phi_C \rangle} .$$

This method reduces to the one used here provided that the target is represented by a single determinant of occupied Hartree-Fock orbitals, χ_a , represented by

$$\Gamma = |D_{HF}^N\rangle ,$$

and the scattering solution is formed by adding s_1 , c_1 , and χ_p to make the $N+1$ electron functions

$$\phi_S = |s_1 D_{HF}^N\rangle ,$$

$$\phi_C = |c_1 D_{HF}^N\rangle ,$$

$$\text{and } \eta_p = |\chi_p D_{HF}^N\rangle ,$$

where χ_p is a virtual Hartree-Fock orbital. Under these conditions the integral $\langle \eta_p | H_{N+1} - E_p | \phi_S \rangle$ reduces to

$$\{ \langle \chi_p | T - \frac{1}{2}k^2 | s_1 \rangle - \langle \chi_p | \frac{N}{r_1} | s_1 \rangle + \sum_{j=1}^N \langle \chi_j \chi_p | | \chi_j s_1 \rangle \} / (N+1)! .$$

This can be immediately recognized as our previous expression.

Yarlagadda et al. (1973) used the same one electron non-local potential equation used here as a starting point but included a correlated self-energy operator. In their treatment Σ is given by

$$\Sigma(x, x'; E) = \Sigma_{HF}(x, x') + \Sigma^<(x, x'; E) + \Sigma^>(x, x'; E) ,$$

where $\Sigma^<$ and $\Sigma^>$ are generalized polarization potentials given in terms of the generalized response function in the random-phase approximation (RPA). By dropping all terms in Σ except Σ_{HF} , the present static-exchange method is obtained. The polarization potential used in this work can be viewed as a local, energy independent approximation to the potential of Yarlagadda et al.

To test the programs that were written for the calculation of Harris phase shifts, a series of tests were performed on the helium atom. This system was chosen because it is a very simple system to obtain target wavefunctions for and because of the wealth of prior work, both theoretical and experimental. In the calculations performed two different basis sets were used for the Hartree-Fock description of the helium atom. The first, called He10, is a ten STO basis comprised of the five optimized STO's of Clementi (1965) plus five more diffuse STO's of higher principal quantum number and the other, called He20, is a twenty STO extension of basis He10. Both of these basis sets are shown in Table 12.

There are several reasons for using extended basis sets. One main reason is that they give more virtual orbitals and energies at

Table 12
Helium Basis Sets

<u>orbital</u>	<u>Basis He10 exponent</u>	<u>Basis He20 exponent</u>
1s	1.4300	1.4300
1s	2.4415	2.4415
1s	4.0996	4.0996
1s	6.4843	6.4843
1s	0.7978	0.7978
1s		0.100
1s		0.050
1s		0.075
1s		0.010
2s	1.000	1.000
2s	0.500	0.500
2s	0.250	0.250
2s		0.100
2s		0.075
2s		0.025
3s	1.000	1.000
3s	0.500	0.500
3s		0.250
3s		0.100
3s		0.050

which phase shifts and cross sections can be calculated. The nature of the basis sets used is such that many of the virtual eigenvalues are clustered at low energies, thereby giving a better description of the shape of the cross section curve in this region. The use of extended basis sets, like those used here, may also improve the calculations by giving a more accurate description of the long range behavior of the static-exchange potential.

Tables 13 and 14 show the static-exchange results obtained with the basis sets mentioned. These results are also shown graphically in Figure 5 and can be seen to agree very well. The discrepancy at low energy can possibly be explained by the better long range description of the helium 1s orbital provided by basis He20.

Figure 6 shows a comparison of the results obtained in this work with some previous calculations.

3.5 Beryllium

Since the ultimate goal of this work is the calculation of shape resonances in the group IIA elements, a likely place to begin is beryllium. From a theoretical standpoint, this is a very good starting point because of its small size. Unfortunately, it is difficult to do the necessary experiments on beryllium because of health hazards.

In the calculations to be described here, Clementi's (1965) extended basis was used to describe the target 1s and 2s orbitals. The virtual orbitals and energies were obtained from three different Hartree-Fock calculations each using a different set of $2p_0$ functions. These basis sets are shown in Table 15. Only p_0 functions were

Table 13
He10 Results

<u>energy (eV)</u>	<u>phase shift (rad)</u>	<u>cross section (au²)</u>
0.1537	3.0136	18.1326
0.7728	3.8155	22.7077
2.3729	2.5609	21.6837
6.1827	2.2320	17.2258
15.3040	1.8277	10.4505
38.7226	1.3881	4.2695
106.7075	0.9928	1.1240
350.8599	0.6607	0.1835
1896.1131	0.3152	0.0087

Table 14
He20 Results

<u>energy (eV)</u>	<u>phase shift (rad)</u>	<u>cross section (au²)</u>
0.0004	3.1350	17.4187
0.0023	3.1243	22.4827
0.0071	3.1097	24.3011
0.0177	3.0905	25.2611
0.0384	3.0655	25.7255
0.0776	3.0329	25.9196
0.1515	2.9895	25.9036
0.2923	2.9304	25.7048
0.5639	2.8489	25.2345
1.0970	2.7355	24.3211
2.1696	2.5771	22.5510
4.3910	2.3578	19.4053
9.1601	2.0652	14.4625
19.9452	1.7040	8.4209
46.5337	1.3127	3.4348
120.9710	0.9571	0.9446
381.3872	0.6457	0.1623
2008.1614	0.3088	0.0079

Figure 5 Plot of phase shift versus energy for helium. The Δ curve was obtained using the He10 basis and the * curve was obtained using the He20 basis.

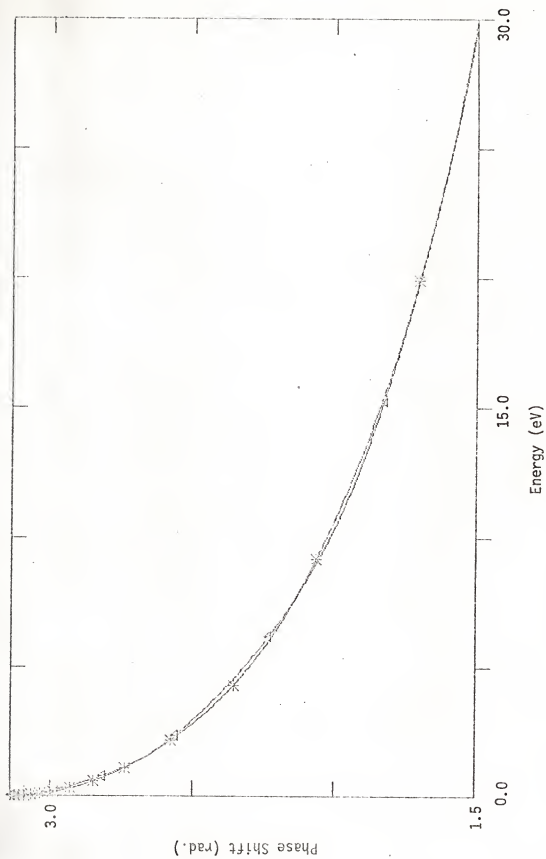


Figure 6 Plot of phase shift versus energy. The curves were obtained from: Harris and Michels (1971) (+); Yariagadda et al. (1973) ($\times$); Present work with He10 basis (Δ); Present work with He20 basis (*).

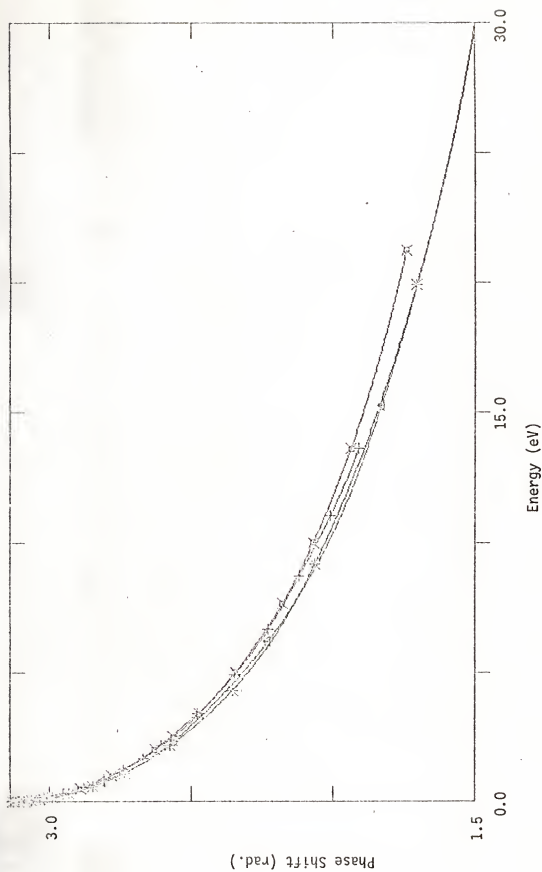


Table 15
Be Basis Functions

Target orbitals			
<u>STO</u>	<u>exponent</u>	<u>1s coef.</u>	<u>2s coef.</u>
1s	3.4703	0.91792	0.17065
1s	6.3631	0.08742	0.01469
2s	0.7516	0.00147	-0.11551
2s	0.9084	-0.00267	-0.67835
2s	1.4236	0.00222	-0.30265
2s	2.7616	0.00597	0.09232

Virtual orbitals			
<u>STO</u>	<u>basis 1</u>	<u>basis 2</u>	<u>basis 3</u>
2p0	1.900	2.000	2.100
2p0	1.400	1.500	1.600
2p0	0.900	1.000	1.100
2p0	0.700	0.750	0.800
2p0	0.450	0.500	0.550
2p0	0.350	0.375	0.400
2p0	0.220	0.250	0.280
2p0	0.170	0.180	0.190
2p0	0.110	0.120	0.130
2p0	0.085	0.090	0.095
2p0	0.055	0.060	0.065
2p0	0.025	0.030	0.035

used because the shape resonance should occur as a $2p$ state and, therefore, will show up only in the p-wave cross section. Three different basis sets were used to provide more virtual orbitals in a useful energy range without doing a very large calculation. One advantage in doing these calculations on beryllium is there are no p_0 orbitals in the occupied Hartree-Fock set of orbitals. Therefore, p_0 functions can be added to the basis or their exponents can be varied and there will be no changes in the static-exchange potential except through the exchange terms which are very small. The results of the calculations are given in Table 16.

Calculations were also performed using the polarization potential mentioned previously. Since this potential has an arbitrary parameter r_0 , some method of arriving at its value is needed. In the work discussed here r_0 is picked as the value at which the potential $(1+1)/2r^2 + V_{p0}$ is zero. The expression for r_0 is then

$$r_0 = \left\{ \frac{\alpha}{1(1+1)} \right\}^{1/2}$$

For beryllium, the static polarizability used is 47 a.u. and r_0 is chosen as 5 Bohrs. The results obtained with the polarization potential included are shown in Table 17. A plot of the low energy portion of the cross section curve is shown in Figure 7 for both the static-exchange and static-exchange + polarization calculations. As can be seen, the addition of the polarization potential causes a dramatic change in the cross section. The reliability of this change is discussed further during the evaluation of the resonance parameters.

Table 16
Be Static-exchange Results

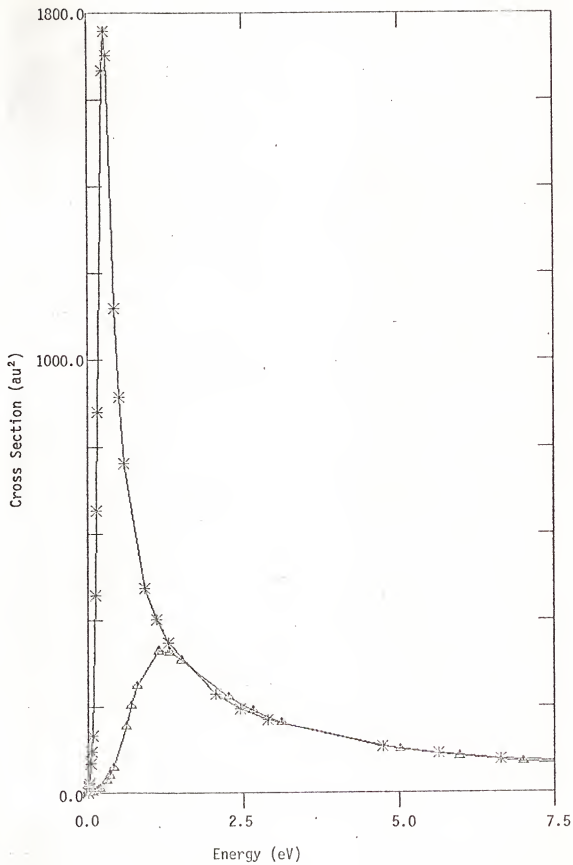
<u>E(eV)</u>	<u>phase shifts (rad.)</u>	<u>cross sections (au²)</u>
0.004202	0.000139	0.002375
0.005451	0.000207	0.004039
0.006798	0.000290	0.006353
0.018394	0.001577	0.069319
0.022614	0.002151	0.104979
0.027191	0.002840	0.152096
0.054174	0.008019	0.608875
0.064984	0.010721	0.907111
0.076655	0.013949	1.301892
0.133786	0.035220	4.753734
0.158757	0.046136	6.872079
0.185447	0.059121	9.655860
0.300029	0.128540	28.090688
0.352412	0.169153	41.247963
0.406992	0.216708	58.263549
0.608721	0.440872	153.435384
0.701153	0.554051	202.499887
0.795346	0.670897	249.247327
1.143305	1.029797	329.638437
1.316582	1.157449	326.720581
1.505334	1.257652	308.394359
2.252472	1.442995	224.010669
2.658461	1.469213	190.950717
3.105742	1.477906	163.727877
5.017304	1.422467	99.995392
5.965638	1.401906	83.548150
6.997279	1.380897	70.689548
11.693033	1.315351	41.064003
13.847953	1.294340	34.279256
16.178037	1.275813	29.024436
30.325205	1.150602	14.098987
35.674818	1.131722	11.779206
41.487912	1.112447	9.942484
99.405096	0.890287	3.117141
117.676441	0.853701	2.476104
137.705365	0.819420	1.988966

Table 17

Be Static-exchange plus Polarization Results

<u>E(eV)</u>	<u>phase shifts (rad.)</u>	<u>cross sections (au²)</u>
0.004192	0.003042	1.132535
0.005435	0.004018	1.523699
0.006773	0.005135	1.996677
0.018233	0.019675	10.888717
0.022364	0.025801	15.263814
0.026821	0.032850	20.628901
0.052723	0.083696	67.988909
0.062787	0.108474	95.746635
0.073415	0.138261	132.703602
0.121498	0.335596	457.866409
0.140120	0.435851	652.437972
0.158628	0.549157	880.948064
0.231334	1.049741	1667.766610
0.261811	1.244082	1757.304698
0.294031	1.415030	1702.425504
0.431053	1.818372	1118.444717
0.503026	1.897914	914.376183
0.582814	1.945246	762.322092
0.921154	1.964526	474.862546
1.098676	1.951096	402.517857
1.292951	1.930785	347.471062
2.050532	1.860148	229.770366
2.454522	1.821383	196.115766
2.895756	1.784643	169.147309
4.731597	1.666117	107.418995
5.639251	1.629738	90.637887
6.625188	1.600228	77.351077
11.208313	1.580295	45.757406
13.366430	1.520797	38.277120
15.710701	1.450245	32.174991
29.944744	1.034357	12.654530
35.301277	1.125939	11.838870
41.124872	1.270586	11.381315
99.174761	1.119829	4.189378
117.456041	1.085710	3.417380
137.493739	0.868290	2.173016

Figure 7 Plot of cross section versus energy for beryllium.
The Δ curve was calculated using the static-exchange
potential and the * curve was calculated using the
static-exchange plus polarization potential.



3.6 Magnesium

The next group IIA element is magnesium and, unlike beryllium, experimental work has been done on it. Unfortunately from a theoretical standpoint, this system is much more difficult to calculate because of its larger number of electrons.

Again, as was done for beryllium, Clementi's (1965) extended basis sets were used to describe the target $1s$, $2s$, $2p$, and $3s$ orbitals. In order to obtain virtual orbitals and energies, this basis was augmented by three different sets of p_0 orbitals. The basis is shown in Table 18. Unlike the beryllium case, where the additional p_0 functions have no effect on the target potential, in magnesium they do. The additional p_0 functions will mix with the occupied $2p_0$ function and cause a slight breaking of the degeneracy of the $2p$ functions. Thus, as the additional p_0 functions are varied the occupied $2p_0$ function changes and, therefore, the potential changes. While in general, this would seem to create problems, in practice the changes are so slight that the potential can be regarded as constant provided no major changes are made in the additional p_0 functions. The results of these static-exchange calculations are shown in Table 19.

Calculations were also done using the polarization potential with $\alpha = 81$. and $r_0 = 6.3$. These results are given in Table 20 and a comparison plot of the cross section with and without the polarization potential is given in Figure 8. Again, notice the dramatic effect of the polarization potential.

Table 18
Magnesium Basis

Target orbitals:

<u>exponent</u>	<u>1s</u>	<u>2s</u>	<u>3s</u>
12.0	0.96539	-0.24382	0.04695
13.5552	0.03767	-0.00504	0.00166
9.2489	0.01583	0.10176	-0.02391
6.5517	-0.00212	0.39908	-0.07764
4.2008	0.00104	0.55719	-0.13548
2.4702	-0.00014	0.04715	-0.00710
1.4331	0.00005	-0.00783	0.50699
0.8783	0.00001	0.00197	0.57016

<u>exponent</u>	<u>2p</u>
6.0	0.51090
7.9884	0.08276
5.3197	0.32223
3.7168	0.21178
2.5354	0.03591

Virtual orbitals:

<u>exponent</u>	<u>np₀</u> (n=3,4,5,6,7)
1.00	all calc.
0.30	basis set 1
0.325	basis set 2
0.35	basis set 3

Table 19
Mg Static-exchange Results

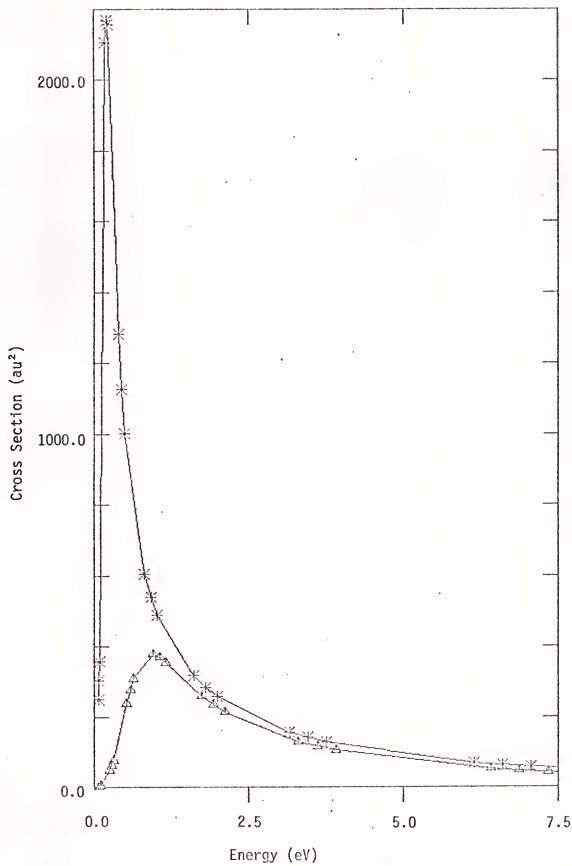
<u>E(eV)</u>	<u>phase shifts (rad.)</u>	<u>cross sections (au²)</u>
0.081827	0.021150	2.803479
0.092882	0.025704	3.647776
0.104139	0.030670	4.631591
0.251770	0.153096	47.377459
0.282524	0.184554	61.136029
0.313107	0.217919	76.568734
0.523734	0.515179	237.727264
0.579667	0.592669	276.075872
0.635199	0.666490	308.626046
0.951745	0.994143	378.713888
1.053091	1.057389	369.561864
1.156575	1.106756	354.638997
1.742237	1.213852	258.454327
1.928260	1.220699	234.703816
2.116931	1.220718	213.788917
3.301539	1.142453	128.551696
3.608436	1.122871	115.479886
3.917077	1.102427	104.257131
6.404669	0.931352	51.565066
6.869169	0.908184	46.410493
7.338163	0.885543	41.901138
12.695070	0.651735	14.864938
13.393855	0.631349	13.340873
14.106339	0.611290	11.976657
26.702131	0.357590	2.353288
27.871870	0.339243	2.037852
29.076516	0.320871	1.754699
70.411131	2.956181	0.247567
73.122476	2.935589	0.293486
75.936550	2.914877	0.341272

Table 20

Mg Static-exchange plus Polarization Results

<u>E(eV)</u>	<u>phase shifts (rad.)</u>	<u>cross sections (au²)</u>
0.071849	0.187897	249.080902
0.079643	0.218614	302.912990
0.087114	0.249523	359.038448
0.181427	1.041606	2106.574817
0.198396	1.157026	2167.357707
0.215599	1.259715	2156.112829
0.387777	1.745007	1282.953281
0.436002	1.776453	1127.335632
0.485986	1.794933	1003.262067
0.808969	1.788866	604.353123
0.912347	1.770552	540.051458
1.018105	1.749677	487.839174
1.612432	1.618644	317.369196
1.801153	1.584771	284.711727
1.991531	1.552758	257.461588
3.154180	1.381273	156.841341
3.458330	1.351105	141.267270
3.763056	1.322886	128.094564
6.144810	1.133358	68.491260
6.600492	1.107281	62.174431
7.061153	1.081434	56.588127
12.352179	0.782344	20.635094
13.054273	0.756306	18.502856
13.769579	0.730963	16.601043
26.396296	0.413249	3.133697
27.567770	0.393949	2.741167
28.774576	0.373839	2.377253
70.227328	2.932335	0.315174
72.940730	2.901953	0.396148
75.756894	2.889071	0.422635

Figure 8 Plot of cross section versus energy for magnesium.
The Δ curve was calculated using the static-exchange
potential and the * curve was calculated using the
static-exchange plus polarization potential.



3.7 Evaluation of Resonance Parameters

The shape of the cross sections for Be and Mg given in Figures 7 and 8 shows evidence for the existence of a resonance but from them it is not obvious how to obtain the resonance parameters. These parameters are the resonance energy E_r and the width Γ . To evaluate E_r and Γ it is easier to consider the shape of the phase shift curves. Figure 9 shows a plot of δ versus E for Be and Figure 10 shows a similar plot for Mg.

One way of obtaining resonance information via phase shifts is through a study of time delay (Bohm, 1951; Wigner, 1955). The time delay of an outgoing particle due to the presence of a potential is given by

$$\Delta t = 2\hbar \frac{d\delta}{dE}.$$

The energy of maximum time delay is identified as the resonance energy and the resonance width is then given as

$$\frac{2}{\Gamma} = \left. \frac{d\delta}{dE} \right|_{E=E_r}.$$

To actually solve for the values of E_r and Γ from the phase shift curves, the values of the first and second derivative curves are needed. The second derivative is used because it is simpler to find the zero of it than the maximum of the first derivative. In order to evaluate the derivative curves some form must be chosen for the phase shift curve. In this work a cubic spline was used to fit the phase shift values. First and second derivatives are then evaluated at the known energies and these quantities are also fit via cubic splines to provide continuous curves.

Figure 9 Plot of phase shift versus energy for beryllium. The Δ curve is from calculations using the static-exchange potential and the * curve is from calculations using the static-exchange plus polarization potential.

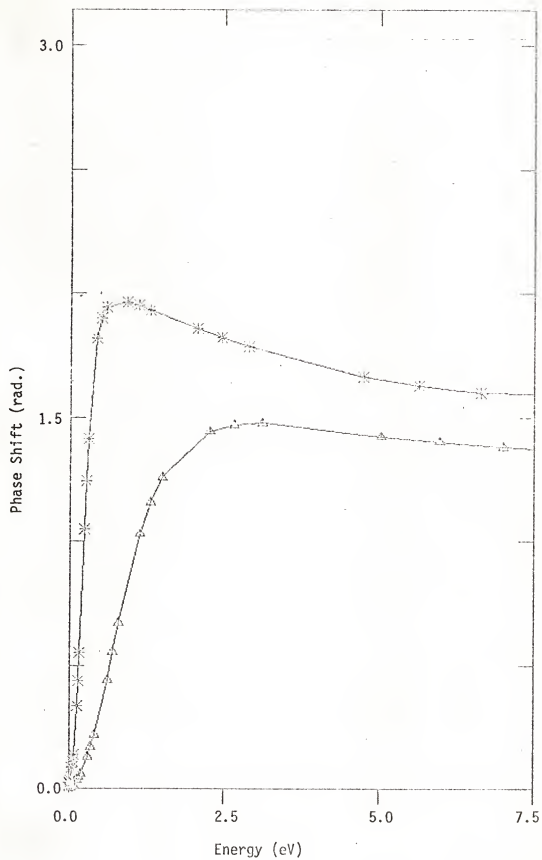
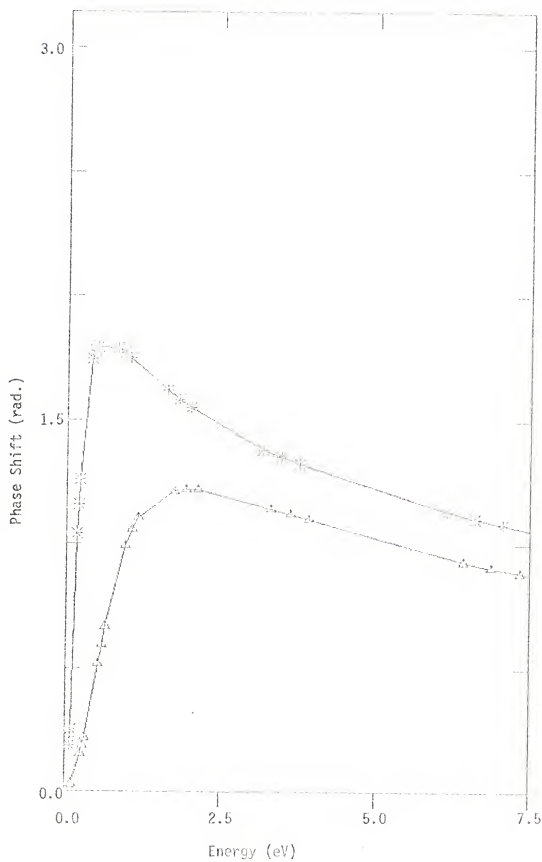


Figure 10 Plot of phase shift versus energy for magnesium. The Δ curve is from calculations using the static-exchange potential and the * curve is from calculations using the static-exchange plus polarization potential.



The resonance parameters obtained from the Be and Mg calculations are shown in Table 21. Also given in this table are the experimental results of Burrow et al. (1976) and the model potential results of Hunt and Moiseiwitsch (1970). The first thing that should be noticed is the large change in the parameters when the polarization potential is added. Because of this, it is obvious that for the systems studied here polarization effects are extremely important. These effects can not be ignored if accurate values are sought.

With the polarization potential used in this work, it is not possible to evaluate the quality of the effects included. This is because the potential depends on the parameter r_0 and no completely justifiable method for obtaining its value is given. Further studies should be made to explore how the effects change as r_0 changes and also to explore other types of polarization potentials.

Table 21
Resonance Parameters

	<u>static- exchange</u>	<u>s-e plus V_{pol}</u>	<u>H&M^a</u>	<u>Exp.^b</u>
Be E _r	0.769	0.195	0.60	---
Γ	1.611	0.283	0.22	---
Mg E _r	0.460	0.161	0.37	0.15
Γ	1.374	0.238	0.10	0.14

^aHunt and Moiseiwitsch (1970)

^bBurrow et al. (1976)

APPENDIX A THIRD ORDER RSPT ON THE Δ SCF IONIZATION ENERGY

As was previously stated, the Δ SCF ionization energy is the difference between two Hartree-Fock energies. If we use the notation that j and ϵ_j ("untilded" quantities) are the Hartree-Fock orbitals and orbital energies of the N electron state and $\tilde{j}$ and $\tilde{\epsilon}_j$ ("tilded" quantities) are the same for the $N-1$ electron state, we obtain the following expression for the ionization energy

$$\begin{aligned} -I(\Delta\text{SCF}) &= E_{\text{HF}}^N - E_{\text{HF},x}^{N-1} \\ &= \left\{ \sum_a \epsilon_a - \frac{1}{2} \sum_{a,b} \langle ab || ab \rangle \right\} - \left\{ \sum_{a \neq x} \tilde{\epsilon}_a - \frac{1}{2} \sum_{a,b \neq x} \langle \tilde{a} \tilde{b} || \tilde{a} \tilde{b} \rangle \right\} \\ &= \epsilon_x + \sum_{a \neq x} (\epsilon_a - \tilde{\epsilon}_a) - \sum_{a \neq x} \langle ax || ax \rangle - \frac{1}{2} \sum_{a,b \neq x} \{ \langle ab || ab \rangle - \langle \tilde{a} \tilde{b} || \tilde{a} \tilde{b} \rangle \}. \end{aligned}$$

In the preceding equation, as throughout the paper, the notation used is: a,b,c,d = occupied spin orbitals; p,q,r,s = unoccupied spin orbitals; i,j,k,l = unspecified spin orbitals.

By assuming the N electron Hartree-Fock ground state to be the reference state for a perturbation expansion of the $N-1$ electron state, we arrive at the following expression for the ionization energy through third order

$$\begin{aligned} -I(\Delta\text{SCF}) &= \epsilon_x - \sum_{a \neq x} \{ \epsilon_a^{(1)} - \epsilon_a^{(2)} - \epsilon_a^{(3)} \} - \sum_{a \neq x} \langle ax || ax \rangle \\ &\quad + \sum_{a,b \neq x} \{ \langle a^{(1)} b || ab \rangle + \langle ab || a^{(1)} b \rangle + \langle a^{(2)} b || ab \rangle \\ &\quad + \langle ab || a^{(2)} b \rangle + \langle a^{(1)} b || a^{(1)} b \rangle \} \end{aligned}$$

$$\begin{aligned}
& + \sum_{a,b \neq x} \{ \langle a^{(1)} b^{(1)} | | ab \rangle + \langle ab | | a^{(1)} b^{(1)} \rangle \\
& + \langle a^{(1)} b | | ab^{(1)} \rangle + \langle ab^{(1)} | | a^{(1)} b \rangle \} .
\end{aligned}$$

Now in order to evaluate the corrections to the orbitals and orbital energies, we must consider the relation between the N electron state Fock operator and the N-1 electron state Fock operator

$$\begin{aligned}
F^N &= h_0 + \sum_a \langle a | | a \rangle \\
\text{and} \quad F_x^{N-1} &= h_0 + \sum_{a \neq x} \langle \tilde{a} | | \tilde{a} \rangle ,
\end{aligned}$$

where x is the label of the removed spin orbital and where $\langle i | | i \rangle$ stands for the coulomb minus exchange operator. This gives the relation

$$F_x^{N-1} = F^N - \langle x | | x \rangle + \sum_{a \neq x} \{ \langle \tilde{a} | | \tilde{a} \rangle - \langle a | | a \rangle \} .$$

The perturbation is given by $V_1 + V_2$, where $V_1 = -\langle x | | x \rangle$ and $V_2 = \sum_{a \neq x} \{ \langle \tilde{a} | | \tilde{a} \rangle - \langle a | | a \rangle \}$. The perturbation V_2 is somewhat unusual because it is defined in terms of both unperturbed and perturbed orbitals. Therefore, to obtain expression up to a given order in electron interaction we must apply our perturbation in an iterative fashion.

Before we apply this result to the expression for the ionization energy, we can simplify the expression by noting that

$$\begin{aligned}
\sum_{a \neq x} \epsilon_a^{(1)} &= \sum_{a \neq x} \langle a | V | a \rangle = - \sum_{a \neq x} \langle ax | | ax \rangle + \sum_{a,b \neq x} \{ \langle \tilde{a} \tilde{b} | | \tilde{a} \tilde{b} \rangle - \langle ab | | ab \rangle \} \\
&= - \sum_{a \neq x} \langle ax | | ax \rangle + \sum_{a,b \neq x} \{ \langle ab^{(1)} | | ab \rangle + \langle ab | | ab^{(1)} \rangle \\
&\quad + \langle ab^{(2)} | | ab \rangle + \langle ab | | ab^{(2)} \rangle + \langle ab^{(1)} | | ab^{(1)} \rangle \} .
\end{aligned}$$

This cancels some of our previous terms and leaves

$$-I(\Delta SCF) = \epsilon_X - \sum_{a \neq X} \{ \epsilon_a^{(2)} + \epsilon_a^{(3)} \} + \frac{1}{2} \sum_{a, b \neq X} \{ \langle a^{(1)} b^{(1)} | | ab \rangle + \langle a^{(1)} b | | ab^{(1)} \rangle + \langle ab | | a^{(1)} b^{(1)} \rangle + \langle ab^{(1)} | | a^{(1)} b \rangle \}.$$

To illustrate how to deal with the perturbation, we shall work through an example in detail. Let us consider the case of the second order energy correction

$$\sum_{a \neq X} \epsilon_a^{(2)} = - \sum_{\substack{a \neq X \\ k \neq a}} \frac{\langle a | V | k \rangle \langle k | V | a \rangle}{(\epsilon_k - \epsilon_a)}$$

Substituting the perturbation we get

$$- \sum_{\substack{a \neq X \\ k \neq a}} \frac{|\langle ax | | kx \rangle|^2}{\epsilon_k - \epsilon_a} \quad (V_1:V_1 \text{ term})$$

$$+ \sum_{\substack{a \neq X \\ k \neq a}} \frac{\langle ax | | kx \rangle \{ \langle kb | | ab \rangle - \langle kb | | ab \rangle \}}{\epsilon_k - \epsilon_a} \quad (V_1:V_2 \text{ term})$$

$$+ \sum_{\substack{a \neq X \\ k \neq a}} \frac{\{ \langle ab | | kb \rangle - \langle ab | | kb \rangle \} \langle kx | | ax \rangle}{\epsilon_k - \epsilon_a} \quad (V_2:V_1 \text{ term})$$

Using the expansion for b and keeping terms through third order we now obtain

$$\begin{aligned} & - \sum_{\substack{a \neq X \\ k \neq a}} \frac{|\langle ax | | kx \rangle|^2}{\epsilon_k - \epsilon_a} + \sum_{\substack{a, b \neq X \\ k \neq a}} \frac{\{ \langle ax | | kx \rangle \langle kb^{(1)} | | ab \rangle + \langle ax | | kx \rangle \langle kb | | ab^{(1)} \rangle \}}{\epsilon_k - \epsilon_a} \\ & + \sum_{\substack{a, b \neq X \\ k \neq a}} \frac{\{ \langle ab^{(1)} | | kb \rangle \langle kx | | ax \rangle + \langle ab | | kb^{(1)} \rangle \langle kx | | ax \rangle \}}{\epsilon_k - \epsilon_a} \end{aligned}$$

$$\begin{aligned}
&= -\sum_{\substack{a \neq x \\ k \neq a}} \frac{|\langle ax || kx \rangle|^2}{\epsilon_k - \epsilon_a} \\
&+ \sum_{\substack{a, b \neq x \\ k \neq a \\ l \neq b}} \left\{ \frac{\langle ax || kx \rangle \langle kl || ab \rangle \langle bx || lx \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} + \frac{\langle ax || kx \rangle \langle kb || al \rangle \langle lx || bx \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} \right. \\
&\quad \left. + \frac{\langle al || kb \rangle \langle bx || lx \rangle \langle kx || ax \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} + \frac{\langle ab || kl \rangle \langle lx || bx \rangle \langle kx || ax \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} \right\}.
\end{aligned}$$

Similarly, we obtain from the other parts of the ionization energy expression the following terms

$$\sum_{a \neq x} \epsilon_a^{(3)} = -\sum_{\substack{a \neq x \\ l, k \neq a}} \frac{\langle lx || kx \rangle \langle kx || ax \rangle \langle ax || lx \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_a)} + \sum_{\substack{a \neq x \\ l \neq a}} \frac{\langle lx || ax \rangle \langle ax || ax \rangle \langle ax || lx \rangle}{(\epsilon_l - \epsilon_a)^2}$$

and

$$\begin{aligned}
&{}_{1/2} \sum_{a, b \neq x} \{ \langle a^{(1)} b^{(1)} || ab \rangle + \langle a^{(1)} b || ab^{(1)} \rangle + \langle ab || a^{(1)} b^{(1)} \rangle + \langle ab^{(1)} || a^{(1)} b \rangle \} \\
&= {}_{1/2} \sum_{\substack{a, b \neq x \\ k \neq a \\ l \neq b}} \left\{ \frac{\langle kl || ab \rangle \langle ax || kx \rangle \langle bx || lx \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} + \frac{\langle ab || kl \rangle \langle kx || ax \rangle \langle lx || bx \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} \right. \\
&\quad \left. + \frac{\langle kb || al \rangle \langle ax || kx \rangle \langle lx || bx \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} + \frac{\langle al || kb \rangle \langle bx || lx \rangle \langle kx || ax \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} \right\}.
\end{aligned}$$

Now by combining the terms we have obtained, we arrive at the expression for the ionization energy at the Δ SCF level through third order in electron interaction.

$$\begin{aligned}
-I(\Delta\text{SCF}) &= \epsilon_x + \sum_{\substack{a \neq x \\ k \neq a}} \frac{|\langle ax || kx \rangle|^2}{\epsilon_k - \epsilon_a} \\
&- {}_{1/2} \sum_{\substack{a, b \neq x \\ k \neq a \\ l \neq b}} \left\{ \frac{\langle ax || kx \rangle \langle kl || ab \rangle \langle bx || lx \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} + \frac{\langle ax || kx \rangle \langle kb || al \rangle \langle lx || bx \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} \right. \\
&\quad \left. + \frac{\langle al || kb \rangle \langle bx || lx \rangle \langle kx || ax \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} + \frac{\langle ab || kl \rangle \langle lx || bx \rangle \langle kx || ax \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} \right\}.
\end{aligned}$$

$$+ \sum_{\substack{a \neq x \\ l, k \neq a}} \frac{\langle l x | | k x \rangle \langle k x | | a x \rangle \langle a x | | l x \rangle}{(\epsilon_k - \epsilon_a)(\epsilon_l - \epsilon_b)} - \sum_{\substack{a \neq x \\ l \neq a}} \frac{\langle l x | | a x \rangle \langle a x | | a x \rangle \langle a x | | l x \rangle}{(\epsilon_l - \epsilon_a)^2} .$$

APPENDIX B THIRD ORDER RSPT ON THE TOM IONIZATION ENERGY

The TOM ionization energy is given by the eigenvalue ϵ_x of the transition operator defined by

$$F_x^T = h_0 + \sum_{a \neq x} \langle \tilde{a} | | \tilde{a} \rangle + \frac{1}{2} \langle \tilde{x} | | \tilde{x} \rangle .$$

In this section we will obtain an expression for $\tilde{\epsilon}_x$ by using RSPT with the Hartree-Fock N electron ground state as our reference. In order to define the perturbation, we must consider the relation between the Fock operators

$$F_x^T = F_{HF}^N - \langle x | | x \rangle + \frac{1}{2} \langle \tilde{x} | | \tilde{x} \rangle + \sum_{a \neq x} \{ \langle \tilde{a} | | \tilde{a} \rangle - \langle a | | a \rangle \} .$$

Keeping all terms through third order, the perturbation V can be expressed as

$$\begin{aligned} V &= - \langle x | | x \rangle + \frac{1}{2} \langle \tilde{x} | | \tilde{x} \rangle + \sum_{a \neq x} \{ \langle \tilde{a} | | \tilde{a} \rangle - \langle a | | a \rangle \} \\ &= -\frac{1}{2} \langle x | | x \rangle + \sum_{a \neq x} \{ \langle a^{(1)} | | a \rangle + \langle a | | a^{(1)} \rangle + \langle a^{(1)} | | a^{(1)} \rangle \\ &\quad + \langle a^{(2)} | | a \rangle + \langle a | | a^{(2)} \rangle \} . \end{aligned}$$

Now we can proceed to evaluate $\epsilon_x = \epsilon_x + \epsilon_x^{(1)} + \epsilon_x^{(2)} + \epsilon_x^{(3)}$. First let us consider $\epsilon_x^{(1)}$.

$$\begin{aligned} \epsilon_x^{(1)} &= \langle x | V | x \rangle \\ &= -\frac{1}{2} \langle xx | | xx \rangle + \sum_{a \neq x} \{ \langle xa^{(1)} | | xa \rangle + \langle xa | | xa^{(2)} \rangle \\ &\quad + \langle xa^{(1)} | | xa^{(1)} \rangle + \langle xa | | xa^{(1)} \rangle + \langle xa^{(2)} | | xa \rangle \} . \end{aligned}$$

Using the expressions for $a^{(1)}$ and $a^{(2)}$,

$$a^{(1)} = - \sum_{l \neq a} \frac{l \langle l | V | a \rangle}{\epsilon_l - \epsilon_a}$$

$$a^{(2)} = \sum_{l, k \neq a} \frac{l \langle l | V | k \rangle \langle k | V | a \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_a)} - \sum_{l \neq a} \frac{l \langle l | V | a \rangle \langle a | V | a \rangle}{(\epsilon_l - \epsilon_a)^2} - \frac{1}{2} \sum_{l \neq a} \frac{a \langle a | V | l \rangle \langle l | V | a \rangle}{(\epsilon_l - \epsilon_a)^2},$$

we obtain

$$\begin{aligned} x^{(1)} = & - \sum_{\substack{a \neq x \\ l \neq a}} \left\{ \frac{\langle x l | | x a \rangle \langle a | V | l \rangle}{(\epsilon_l - \epsilon_a)} + \frac{\langle x a | | x l \rangle \langle l | V | a \rangle}{(\epsilon_l - \epsilon_a)} \right\} \\ & + \sum_{\substack{a \neq x \\ l, k \neq a}} \frac{\langle x l | | x k \rangle \langle k | V | a \rangle \langle a | V | l \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_a)} \\ & + \sum_{\substack{a \neq x \\ l, k \neq a}} \left\{ \frac{\langle x l | | x a \rangle \langle a | V | k \rangle \langle k | V | l \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_a)} + \frac{\langle x a | | x l \rangle \langle l | V | k \rangle \langle k | V | a \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_a)} \right\} \\ & - \sum_{\substack{a \neq x \\ l \neq a}} \left\{ \frac{\langle x l | | x a \rangle \langle a | V | a \rangle \langle a | V | l \rangle}{(\epsilon_l - \epsilon_a)^2} + \frac{\langle x a | | x l \rangle \langle l | V | a \rangle \langle a | V | a \rangle}{(\epsilon_l - \epsilon_a)^2} \right\} \\ & - \frac{1}{2} \sum_{\substack{a \neq x \\ l \neq a}} \left\{ \frac{\langle x a | | x a \rangle \langle a | V | l \rangle \langle l | V | a \rangle}{(\epsilon_l - \epsilon_a)^2} + \frac{\langle x a | | x a \rangle \langle a | V | l \rangle \langle l | V | a \rangle}{(\epsilon_l - \epsilon_a)^2} \right\}. \end{aligned}$$

If at this point we note that $\epsilon_x^{(2)}$ and $\epsilon_x^{(3)}$ are zero through third order, we see that by adding ϵ_x to $\epsilon_x^{(1)}$ and substituting for V , we arrive at the expression for $\tilde{\epsilon}_x$.

$$\begin{aligned} \tilde{\epsilon}_x = & \epsilon_x + \sum_{\substack{a \neq x \\ l \neq a}} \frac{| \langle x l | | x a \rangle |^2}{\epsilon_l - \epsilon_a} \\ & - \frac{1}{2} \sum_{\substack{a, b \neq x \\ l \neq a \\ k \neq b}} \left\{ \frac{\langle x l | | x a \rangle \langle a k | | l b \rangle \langle b x | | k x \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_b)} + \frac{\langle x l | | x a \rangle \langle a b | | l k \rangle \langle k x | | b x \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_b)} \right. \\ & \left. + \frac{\langle x a | | x l \rangle \langle l k | | a b \rangle \langle b x | | k x \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_b)} + \frac{\langle x a | | x l \rangle \langle l b | | a k \rangle \langle k x | | b x \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_b)} \right\} \end{aligned}$$

$$\begin{aligned}
& + \frac{3}{4} \sum_{\substack{a \neq x \\ l, k \neq a}} \frac{\langle x l | | x a \rangle \langle a x | | k x \rangle \langle k x | | l x \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_a)} \\
& - \frac{3}{4} \sum_{\substack{a \neq x \\ l \neq a}} \frac{\langle x a | | x a \rangle \langle a x | | l x \rangle \langle l x | | a x \rangle}{(\epsilon_l - \epsilon_a)^2} .
\end{aligned}$$

APPENDIX C EXPANSION OF Δ SCF ENERGY IN TERMS OF TOM QUANTITIES

In order to expand the Δ SCF ionization energy in terms of the TOM orbitals and orbital energies, we shall first expand E^N and E_X^{N-1} in terms of the TOM quantities and then subtract the expressions obtained.

Expansion of E^N

In this section quantities with a tilde will represent the N electron state Hartree-Fock solutions. The expression for the total energy is

$$E^N = \sum_a \tilde{\epsilon}_a - \frac{1}{2} \sum_{a,b} \langle \tilde{a} \tilde{b} | | \tilde{a} \tilde{b} \rangle$$

and the perturbation to be used is defined by

$$F^N = F_X^T + \frac{1}{2} \langle X | | X \rangle + \sum_{a \neq x} \{ \langle \tilde{a} | | \tilde{a} \rangle - \langle a | | a \rangle \} .$$

Therefore, the expression for E^N through third order is

$$\begin{aligned} E^N = & \sum_a \{ \epsilon_a + \epsilon_a^{(1)} + \epsilon_a^{(2)} + \epsilon_a^{(3)} \} \\ & - \frac{1}{2} \sum_{a,b} \{ \langle ab | | ab \rangle + \langle a^{(1)}_b | | ab \rangle + \langle ab | | a^{(1)}_b \rangle \\ & + \langle ab | | ab^{(1)} \rangle + \langle ab^{(1)} | | ab \rangle + \langle a^{(2)}_b | | ab \rangle \\ & + \langle ab | | a^{(2)}_b \rangle + \langle ab^{(2)} | | ab \rangle + \langle ab | | ab^{(2)} \rangle \\ & + \langle a^{(1)}_b | | a^{(1)}_b \rangle + \langle ab^{(1)} | | ab^{(1)} \rangle + \langle a^{(1)}_b | | ab^{(1)} \rangle \} \end{aligned}$$

$$+ \langle ab^{(1)} || a^{(1)} b \rangle + \langle a^{(1)} b^{(1)} || ab \rangle + \langle ab || a^{(1)} b^{(1)} \rangle \}$$

Using the expression for $\epsilon_x^{(1)}$ to simplify, we arrive at

$$\begin{aligned} E^N = \sum_a \{ \epsilon_a + \epsilon_a^{(2)} + \epsilon_a^{(3)} \} + \frac{1}{2} \langle ax || ax \rangle - \frac{1}{2} \sum_{a,b} \langle ab || ab \rangle \\ - \frac{1}{2} \sum_{a,b} \{ \langle a^{(1)} b^{(1)} || ab \rangle + \langle ab || a^{(1)} b^{(1)} \rangle + \langle a^{(1)} b || ab^{(1)} \rangle \\ + \langle ab^{(1)} || a^{(1)} b \rangle \} . \end{aligned}$$

Expansion of E_x^{N-1}

The expression for E_x^{N-1} is given by

$$E_x^{N-1} = \sum_{a \neq x} \tilde{\epsilon}_a - \frac{1}{2} \sum_{a,b \neq x} \langle \tilde{a} \tilde{b} || \tilde{a} \tilde{b} \rangle ,$$

where the tilded quantities now refer to the N-1 electron state Hartree-Fock solutions. The perturbation is now defined by

$$F_x^{N-1} = F_x^T - \frac{1}{2} \langle x || x \rangle + \sum_{a \neq x} \{ \langle \tilde{a} || \tilde{a} \rangle - \langle a || a \rangle \} .$$

Following the procedure used for E^N , we obtain

$$\begin{aligned} E_x^{N-1} = \sum_{a \neq x} \{ \epsilon_a + \epsilon_a^{(2)} + \epsilon_a^{(3)} \} - \frac{1}{2} \langle ax || ax \rangle - \frac{1}{2} \sum_{a,b \neq x} \langle ab || ab \rangle \\ - \frac{1}{2} \sum_{a,b \neq x} \{ \langle a^{(1)} b^{(1)} || ab \rangle + \langle ab || a^{(1)} b^{(1)} \rangle + \langle a^{(1)} b || ab^{(1)} \rangle \\ + \langle ab^{(1)} || a^{(1)} b \rangle \} . \end{aligned}$$

Difference $E^N - E_x^{N-1}$

In considering the difference between the equations for E^N and E_x^{N-1} , we see the leading terms give ϵ_x and all first order terms cancel. If we also note that the leading term in the perturbation, V_1 , is $\frac{1}{2} \langle x || x \rangle$ for the N electron energy and $-\frac{1}{2} \langle x || x \rangle$ for the N-1 electron energy, we immediately see that the four intergral terms of

each expression cancel. The expression for $\epsilon_a^{(2)}$ in terms of V_1 is

$$-\sum_{l \neq a}^a \frac{|\langle a|V_1|l \rangle|^2}{\epsilon_l - \epsilon_a} + \sum_{\substack{a,b \\ l \neq a \\ k \neq b}} \frac{\langle a|V_1|l \rangle \{ \frac{\langle l k | ab \rangle \langle b|V_1|k \rangle}{(\epsilon_k - \epsilon_b)} + \frac{\langle l b | ak \rangle \langle k|V_1|b \rangle}{(\epsilon_k - \epsilon_b)} \} }{(\epsilon_l - \epsilon_a)}$$

From this we can see that V_1 will appear an even number of times and, therefore, the terms in $\epsilon_a^{(2)}$ cancel.

This leaves only terms in $\epsilon_a^{(3)}$ to be considered. The expression for $\epsilon_a^{(3)}$ is

$$\sum_{l,k \neq a}^a \frac{\langle l|V_1|k \rangle \langle k|V_1|a \rangle \langle a|V_1|l \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_a)} - \sum_{l \neq a}^a \frac{\langle l|V_1|a \rangle \langle a|V_1|a \rangle \langle a|V_1|l \rangle}{(\epsilon_l - \epsilon_a)^2}$$

Since there is an odd number of V_1 's in $\epsilon_a^{(3)}$, the terms in the N and $N-1$ electron energy expressions will not cancel as previous terms had but will add together.

The result for the differences is then

$$\begin{aligned} -I(\Delta SCF) &= E^N - E_x^{N-1} \\ &= \epsilon_x + \frac{1}{2} \sum_a \sum_{l,k \neq a} \frac{\langle l x | k x \rangle \langle k x | a x \rangle \langle a x | l x \rangle}{(\epsilon_l - \epsilon_a)(\epsilon_k - \epsilon_a)} \\ &\quad - \frac{1}{2} \sum_a \sum_{l \neq a} \frac{\langle l x | a x \rangle \langle a x | a x \rangle \langle a x | l x \rangle}{(\epsilon_l - \epsilon_a)^2} \end{aligned}$$

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BIOGRAPHICAL SKETCH

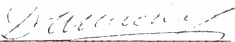
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



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December 1977

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